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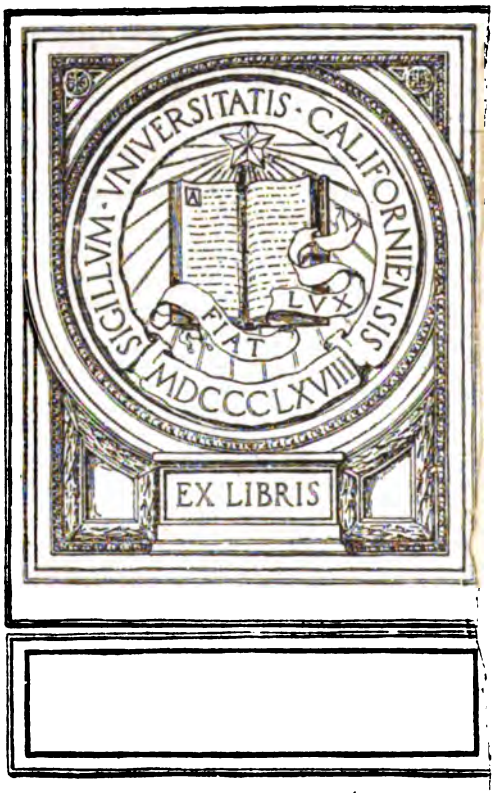

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RECENT ADVANCES IN PHYSICAL AND INORGANIC CHEMISTRY

BY

A. W. STEWART, D.Sc.

LECTURER ON ORGANIC CHEMISTRY IN THE UNIVERSITY OF BELFAST
FORMERLY 1851 EXHIBITION RESEARCH SCHOLAR AND CARNEGIE RESEARCH FELLOW

WITH AN INTRODUCTION BY
SIR WILLIAM RAMSAY, K.C.B., F.R.S.

SECOND EDITION

WITH DIAGRAMS

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PREFACE TO THE FIRST EDITION

UNTIL a few years ago, most chemical text-books were written on the lines laid down by Regnault: the advanced work differed from the elementary manual in the amount of matter which it contained rather than in the manner in which the material was handled. In recent years, however, a certain change has come over chemical literature; and this has been specially marked in the organic branch of the subject. In place of making the advanced book merely an expansion of the elementary one, some writers have endeavoured to break away from the tradition and write series of essays upon various special branches of a subject instead of attempting to force the theoretical and systematic portions into a rigid mould. The present work is an attempt to treat some parts of inorganic and physical chemistry on these lines.

The volume is to some extent a complement to my *Recent Advances in Organic Chemistry*. Like its predecessor, it deals for the most part with researches which have been carried out in the past two decades; but here also no attempt has been made to adhere rigidly to this period when it was desirable to begin the history of a subject at an earlier point. The chief aim kept in view during the preparation of the work was to avoid as far as possible those themes which have been frequently and fully dealt with in text-books; in this way it is hoped that students will find a certain amount of novelty in the subject-matter, whatever may be thought of its treatment.

In a book of this kind, every reader will doubtless detect the omission of some subject in which he is specially interested. It is obviously impossible to include a tithe of the researches which have been carried out in these two branches of chemistry during even the last ten years; and many of the most important investigations have been reluctantly omitted on the ground that a full treatment of them would have occupied more space

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than could be spared, while a partial treatment would have served little purpose. As far as possible, the chapters have been equally divided between inorganic and physical chemistry.

In conclusion, I desire to thank Sir William Ramsay, K.C.B., for the Introduction which he has written for the book, as well as for suggestions and encouragement. I am also greatly indebted to Professor Collie, F.R.S., and Professor Inglis, who have read the manuscript, and given me valuable criticism; to Assistant-Professor Wilsmore, for suggestions with regard to some chapters; and to Assistant-Professor Smiles and Mr. H. T. Clarke, for their trouble in reading the proof-sheets.

A. W. STEWART.

University College, London,
September, 1909.

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PREFACE TO THE SECOND EDITION

In the present edition the material has been rearranged, so that the volume may now roughly be divided into three sections. The first of these, Chapters I. to VI., deals with problems which may be classified as physico-chemical; the next five chapters are concerned with subjects belonging to inorganic chemistry; while the last three chapters of the book give a summary of the phenomena of radioactivity.

Where necessary, the chapters of the previous edition have been rewritten and brought up to date, which in some cases has entailed a very considerable amount of alteration. One chapter of the first edition has been omitted, and in its place an account of the pseudo-acids has been inserted.

As before, footnotes are indicated by asterisks, and references to the literature by numbers; in this way the reader will be saved any unnecessary reference to the foot of the page.

I have again to thank my reviewers for their encouragement and suggestions. Most of the latter have been embodied in the new text.

In the preparation of this edition I have been indebted for assistance to Professors Collie, Inglis, and Wilsmore, and Messrs. Austin, Clarke, and Wright.

A. W. STEWART.

The Sir Donald Currie Laboratories,
The Queen's University of Belfast,
November, 1911.

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CONTENTS

CHAPTER		PAGE
	INTRODUCTION	xiii
I.	DOUBLE SALTS	1
	1. General	1
	2. The Conditions governing the Formation of Double Salts	2
	3. Transition Temperatures	3
	4. Transition Intervals	8
	5. The Existence of Double Salts in Solution	13
	6. Criteria of the Nature of Equimolecular Mixtures of Optical Antipodes	14
II.	THE PROBLEM OF THE OCEANIC SALT DEPOSITS	18
	1. The Stassfurt Salts	18
	2. The Researches of Usiglio and Van't Hoff	19
	3. Solutions of Potassium and Sodium Chlorides	21
	4. The Case of Carnallite	23
	5. The Case of the Chlorides and Sulphates of Magnesium and Potassium	26
	6. The Case of Five Salts	31
	7. The Influence of Time	34
	8. Paragenesis and the Influence of Temperature	35
III.	ABSORPTION SPECTRA	41
	1. General	41
	2. The Hartley Method	47
	3. The Benzene Spectrum	50
	4. The Problem of General Absorption	53
	5. Valency and Absorptive Power	61
	6. The Spectroscopic Determination of Chemical Change	63
	7. Conclusion	64
IV.	THE PSEUDO-ACIDS	69
	1. Introductory	69
	2. Hantzsch's Criteria	74
	3. The Phenomena of Slow Neutralization	76
	4. Abnormal Hydrolysis	77

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CHAPTER PAGE

5. Colour Change in passing from Pseudo-acid to Salt . . . 78
6. Abnormal Temperature Coefficients 80
7. The Ammonia Reaction 81
8. Abnormal Hydrates 82
9. Conductivity in Aqueous-alcoholic Solutions 82
10. The Refractometric Method 83
11. Conclusion 84

V. Colloids 86

1. General 86
2. The Preparation of Colloids 89
3. The Properties of Colloidal Solutions 91
4. Coagulation 97
5. Theories on the Nature of Colloids 99

VI. Reactions in Liquid Ammonia 105

1. The Properties of Liquid Ammonia 105
2. Reactions between Inorganic Salts, Bases, and Acids in Liquid Ammonia Solutions 106
3. The Reactions of Ammono-salts, Ammono-bases and Ammono-acids in Liquid Ammonia Solution 108
4. Ammonolysis 109
5. Other Ionizing Media 110

VII. The Fixation of Nitrogen 113

1. The Circulation of Nitrogen in Nature 113
2. The Production of Nitrogen Oxides, Nitrous and Nitric Acids 115
3. The Production of Ammonia 122
4. The Production of Cyanides 125
5. The Production of Nitrides 128

VIII. Some Hydroxylamine Derivatives 130

1. Introductory 130
2. Nitro-hydroxylaminic Acid 130
3. Nitroxyl 135
4. Ammonia and its Hydroxyl Substitution Products . . . 141

IX. The Cobaltammines 144

1. General 144
2. Theories of the Cobaltammines 145
   (*a*) The Blomstrand-Jörgensen Theory 145
   (*b*) The Werner Hypothesis 151
   (*c*) Friend's Explanation 156
   (*d*) Baker's View 157
   (*e*) Ramsay's Views 158

Digitized by Google

CHAPTER PAGE

3. The Chemical Behaviour of the Cobaltammines 160
(*a*) The Ions in Cobaltammine Solutions 160
(*b*) The Jörgensen-Werner Controversy 165
4. Conclusion 172

X. The Elements of the Rare Earths 176
1. Introductory 176
2. The Importance of the Rare Earths 177
3. The Physical Properties of the Rare Earth Elements . . 177
4. The General Chemical Character of the Rare Earth Elements 178
5. Methods of Preparing and Purifying the Rare Earths . . 180
6. The Place of the Rare Earth Elements in the Periodic System 185

XI. The Inactive Gases 198
1. Historical 198
2. Helium 199
3. Neon 200
4. Argon 201
5. Krypton and Xenon 202

XII. The Radioactive Elements 208
1. Historical 208
2. Radium 205
3. Polonium 210
4. Actinium 211
5. Uranium 212
6. Thorium 212
7. Lead 215
8. Ionium 215
9. Potassium and Rubidium 216

XIII. Radioactive Changes 217
1. The Becquerel Rays 217
2. The Disintegration Hypothesis 224
3. The Origin of Radium 230

XIV. Radioactive Emanations 234
1. The Emanations from Thorium and Actinium 234
2. Niton 235
3. The Production of Helium 243
4. Transmutation 245

Name Index 253

Subject Index 257

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ERRATUM

Page 128, Note 1, *for* " French " *read* " Frank "

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INTRODUCTION

At all periods of the world's history, certain problems have impressed themselves on men's minds as being of paramount importance. History affords many examples of this. From the doctrine of "the divine right of Kings" to the question of "Women's Suffrage" is a long step, but not a longer one than from the once all-absorbing theme which exercised the minds of men of science as regards the true nature of phlogiston, to the present contest regarding the structure of the cobalt-ammines. Science has, however, this advantage over politics —that experiments devised to decide knotty questions are more easily carried out; and, further, that it is in the interests of no one to conceal the truth.

In Dr. Stewart's *Recent Advances in Physical and Inorganic Chemistry*, he has treated of a number of subjects which are at present prominent in the minds of chemists. No doubt they will in time be succeeded by others equally engrossing; the essential features of each of the subjects here considered will have been established or refuted, and new views will in some cases succeed those which he has expounded. Such new views, however, will be the result of maturer knowledge, gained by incessant experiment. At present these essays represent the state of knowledge which we possess; and rival theories have been set forth with fairness, and yet not without some guidance from the author of this work, who has not scrupled to express his own opinion, where he holds a decided view.

The enormous mass of chemical literature which floods our tables monthly makes it almost impossible to do more than glance at the titles of the papers; and each of these, it is sometimes almost sad to think, represents much patient and careful work, which ought to receive, at all events, some consideration. The chemically educated public, too, is rapidly increasing; those who are not themselves actively engaged in furthering the science, and who have neither leisure nor

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inclination to sit down and read the *Transactions of the Chemical Society* or the *Zeitschrift für Anorganische Chemie*, are the better for having their chemical food prepared for the table, instead of trying to assimilate indigestible masses of what is often very crude material. Dr. Stewart may be likened to a skilful cook, who has trimmed his joint, rejecting all innutritious and redundant excrescences, and has served it up to table in a palatable form. Such essays, I venture to think, will do more to encourage a taste for chemistry than many text-books. They will be followed with pleasure by any one who has mastered the nomenclature and is at home with the simpler conceptions of chemistry. Each may be taken to represent in a readable form the latest work on the subject of which it treats.

This book, it may be hoped, will have a still further use; it cannot be doubtful that some who peruse it will have suggested to them various directions in which they may profitably attempt to increase knowledge. Nothing is so sad as to see much time and labour spent, with patience and devotion, in the investigation of some matter which possesses no real importance. It may be retorted that every true statement is of importance, but this is not so. It is only statements which hold forth some prospect of contributing to an organic whole which can be held valuable. There may, perhaps, be a little more merit in ascertaining to the hundredth of a degree the boiling-point of sulphur than of measuring the area of the wings of some particular butterfly; but the difference is barely appreciable. One is as likely to prove useless as the other. It would be well if enthusiasts anxious to carry on research would remember that it is much more stimulating to carry on an interesting than an uninteresting research. It is, I believe, not improbable that the reading of such a work as this may aid those embued with the spirit of investigation to make a happy choice of a subject of research. Should this hope be realized, Dr. Stewart will have done a most useful work.

WILLIAM RAMSAY.

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CHAPTER I

DOUBLE SALTS

1. General

If we dissolve two organic substances or two inorganic salts with a common ion, and then crystallize them from the solution, there are four possible results.

1. The two solutes may separate from the solvent in the form of independent crystals, so that it is possible by mechanical means to separate one substance from the other. In this case we have a *conglomerate.*

2. The crystals which are deposited contain both solutes in quantities depending upon the percentage of each solute present in the solvent. In this case no mechanical separation can be effected, as each separate crystal contains a mixture of the solutes. If we redissolve the crystals, add to the solution more of one of the original solutes, and again crystallize, we shall find that the new crystals have a composition different from that of the first set. In this case we have an example of a *mixed crystal.*

3. The crystals deposited from the solution contain both solutes; but if they are redissolved as in the last example, and some of one solute added to the solution, the crystals which separate from the solution have the same composition as the first set. In this case we have a *double salt* formed.

4. Crystals separate from the solution, and on examination are found to contain portions of both solutes; but if these crystals be redissolved they are found to have acquired new chemical properties, and do not give the reactions of either of the original solutes. In this case we are dealing with a *complex salt.*

We need not enter further into discussions of Cases 1, 2 and 4, which lie outside the limits of the present chapter, but

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must turn to an examination of the class of substances known as double salts.

2. The Conditions governing the Formation of Double Salts

If to a solution of ferrous sulphate we add a solution of magnesium sulphate, we shall find, on evaporating the water, that no double salt is formed from the two sulphates. On the other hand, if we use ammonium sulphate instead of magnesium sulphate, we shall obtain on evaporation crystals of Mohr's salt, $(NH_4)_2SO_4 . FeSO_4 . 6H_2O$. If we employ zinc sulphate and copper sulphate we can obtain no double salt formation; whereas zinc and potassium sulphates together yield the salt $ZnSO_4 . K_2SO_4 . 6H_2O$. It thus becomes evident that the character of the metals from which the salts are derived plays a very considerable part in determining whether or not a given pair of salts will form a double compound with each other.[1]

Retgers states that if two salts can be made to form a series of mixed crystals of varying composition, double salt formation is not to be expected; and, conversely, if two salts combine to form a double salt, we are not likely to obtain a series of mixed crystals from them. For example, ferrous sulphate forms mixed crystals with magnesium sulphate, but no double salt can be obtained from the two; while, on the other hand, potassium and sodium sulphates form no mixed crystals, but do yield a double salt.

Hinrichsen and Sachsel[2] have examined a series of chlorides with respect to double salt formation, with the following results. Ferric chloride and sodium chloride form merely a continuous series of mixed crystals: with potassium chloride at 21° C., ferric chloride gives a double salt, $FeCl_3 . 2KCl . H_2O$: at the same temperature, cæsium chloride and ferric chloride give two double salts, $FeCl_3 . 2CsCl . H_2O$ and $FeCl_3 . 3CsCl . H_2O$. Thus in this case the increase in atomic weight of the metal appears to raise its capacity for double salt formation.

The acid radicles may exert a similar influence; for while

[1] Retgers, *Zeitsch. physikal. Chem.*, 1889, **3**, 289, 497; **4**, 189; **5**, 436; 1890, **6**, 193; 1892, **8**, 6.

[2] Hinrichsen and Sachsel, *Zeitsch. physikal. Chem.*, 1904, **50**, 81.

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sodium chloride forms no double salt with sodium nitrate, the latter body yields a double salt with sodium sulphate.

Physical influences also play a very considerable part in the problem. It has been shown [1] that pressure may be a very important factor in the stability of double salts; while the question of temperature is the dominant feature in any investigation in this department. In the following section we shall deal with this part of the subject.

3. Transition Temperatures

(*a*) *Historical.*—It will be remembered that in the course of his researches on molecular asymmetry, Pasteur,[2] by crystallizing the sodium ammonium salt of racemic acid, was able to obtain two sets of crystals, the one set being the sodium ammonium salt of dextro-tartaric acid, while the others were the corresponding lævo-compound. Staedel,[3] attempting to repeat Pasteur's experiments, found that only the sodium ammonium racemate was formed, no separation of the double salt into its components having taken place. This apparent contradiction found its explanation in the work of Scacchi,[4] who showed that crystallization at high temperatures yields no resolution, while at low temperatures a separation into the two dextro- and lævo-tartrates occurs. The work of Wyrouboff[5] proved that 28° C. was the temperature above which the resolution was not observable.

Now, it has been shown by van't Hoff that this behaviour is characteristic of all double salts: above a certain temperature —to which he gave the name *transition temperature*—the solution of some double salts will yield separate crystals of the two components which go to form it; below the same temperature only the double salt can be obtained. In the case of other double salts, the components are obtained below the transition temperature and the double salt above it. In either case, however, the transition temperature marks the limit of existence

[1] Van't Hoff, *Bildung und Spaltung von Doppelsalzen*, 1897, p. 57.
[2] Pasteur, *Ann. chim. phys.*, 1848, [3] **24**, 442: 1850, [3] **28**, 56.
[3] Staedel, *Ber.*, 1878, **11**, 1752.
[4] Scacchi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1865, 250.
[5] Wyrouboff, *Bull. soc. chim.*, 1884, [2] **41**, 210; 1886, **45**, 52: *Compt. rend.*, 1886, **102**, 627.

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of the two components in solution. Thus we may compare the transition temperature of a double salt to the melting-point of a solid: just as the solid cannot exist above a certain temperature, so some double salts, such as copper dipotassium chloride, when heated above their transition temperature, break down into their components. The case of water of crystallization is, of course, merely an example of double-salt formation. For instance, Glauber's salt has a transition temperature of 32·5° C. If it be heated to this temperature, it loses water and is converted into the anhydrous form—

$$Na_2SO_4 . 10H_2O = Na_2SO_4 + 10H_2O$$

On cooling it below 32·5° C. in presence of water, the anhydrous sodium sulphate will combine with ten molecules of water to form again the original Glauber's salt.

(*b*) *The Determination of Transition Points.*—There are various methods of ascertaining the transition temperature of a substance—

1. The Dilatometric Method.[1]
2. The Tensimetric Method.[2]
3. The Thermometric Method.[3]
4. The Spectrometric Method.
5. The Method of Solubilities.[4]
6. The Method of Electromotive Force Measurements.[5]
7. The Viscosity Method.[6]

We shall take up these in turn.

When a double salt is converted into its components or *vice versâ*, it is to be expected that there will be a sudden change in volume due to the alteration in constitution. If this volume change be sufficiently marked, it forms one of the simplest criteria of the transition temperature. The apparatus employed, the dilatometer, resembles a thermometer with a very large bulb. Into this bulb, the double salt is introduced and covered with oil. The level of the oil is read off on the graduated stem of the dilatometer just as we read off the height of mercury in a thermometer. The bulb of the dilatometer is now placed in a bath whose temperature is very gradually raised. Readings

[1] Van't Hoff, *Bildung und Spaltung von Doppelsalzen*, 1897, p. 33.
[2] *Ibid.*, p. 43. [3] *Ibid.*, p. 55. [4] *Ibid.*, p. 51.
[5] *Ibid.*, p. 48.
[6] Dunstan and Thole, *Trans.*, 1908, **93**, 1815.

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are taken simultaneously of the bath temperature and the height of the oil-level in the stem. At first there will be a steady rise proportional to the temperature; but when the transition point is reached there will naturally be a rapid change in volume of the salt, quite independent of the normal increase in volume of the oil. Thus on plotting the volume against the temperature, we shall obtain a break in the curve at the transition point. Since the transformation of a double salt into its components, or the reverse process, is not instantaneous, there is usually a slight lag in the volume increase. To allow for this it is best to make two sets of measurements, one with a rising, the other with a falling temperature. The two errors then counteract each other to some extent. A modification of the method allows this lag to be turned to account. If we place a mixture of a double salt and the two components in the dilatometer, equilibrium will not be established immediately. The dilatometer bulb is therefore placed in a bath and allowed to attain constant temperature; after which readings of the oil-level are taken as before. Now, unless the temperature of the bath is the transition temperature, it is obvious that the salt within the bulb will contract or expand in the course of time: for if the temperature is one at which the double salt is stable, then the component will be slowly changing into the double salt; or, conversely, if the double salt is unstable at the temperature of the bath, then it will be converted into a mixture of the components. In either case there will be a change in volume, which will make itself apparent in the alteration of the oil-level in the stem. Suppose a contraction takes place. We note the temperature, and then repeat the operation at another temperature; and continue thus until we find some temperature at which expansion occurs. Now, at the transition temperature, since the components are there in equilibrium with the double salt, it is obvious that no change in volume can occur. Therefore the transition temperature lies between the temperature at which expansion occurs and that at which contraction is observed. By a series of measurements we can narrow the limits between the two temperatures, and thus finally arrive at the transition temperature by a series of trials.

The second method of determining the transition point depends upon the fact that at the transition temperature the

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vapour pressures of the double salt and its components must be in equilibrium. The apparatus usually employed is the Bremer-Frowein tensimeter, whose construction is shown in Fig. 1. The whole apparatus is first carefully dried, and then the two substances whose tensions are to be compared are introduced into *d* and *e* respectively. The substance having the greater vapour pressure is usually introduced into *e*. Olive oil is then passed into the U-tube *c* by means of a fine funnel until it stands about halfway up the U-tube on both sides. The tubes at *f* and *g* are now sealed off, and a mercury pump attached to *h*. The whole apparatus is then evacuated. When the highest possible vacuum is produced, the mercury pump is removed by sealing off the tube at *j*. The apparatus is then placed in an air-bath and its temperature gradually raised. At the transition temperature the surface of the oil in the two arms will reach the same level. Of course this is only an outline of the method; numerous precautions must be taken, and some corrections have to be applied in order to make it accurate.

If we allow the temperature of ice to rise slowly, it will be remembered that when it reaches 0° C. a thermometer immersed in it will remain constant until the ice has melted. Applying the analogy between the transition temperature and the melting-point, we arrive at another method of determining the transition temperature. We have only to note the temperature at which a thermometer seems to lag when the mass of double salt surrounding it is slowly heated or cooled through its transition temperature.

The fourth method of determining transition points depends upon the change of colour which some salts undergo at the transition temperature. For instance, a concentrated solution of the two simple salts, ferric chloride and potassium chloride, will be yellow at ordinary temperatures. If it be raised to about 22° C., the colour changes to red,[1] owing to the formation of the double salt $FeCl_3 . 2KCl . H_2O$. This method might be employed even in cases where there is no visible change of colour, by using a photographic spectroscope and noting the change in the ultra-violet spectrum.

At the transition temperature, the solubilities of a double salt and its components become equal; and this has been

[1] Hinrichsen and Sachsel, *Zeitsch. physikal. Chem.*, 1904, 50, 90.

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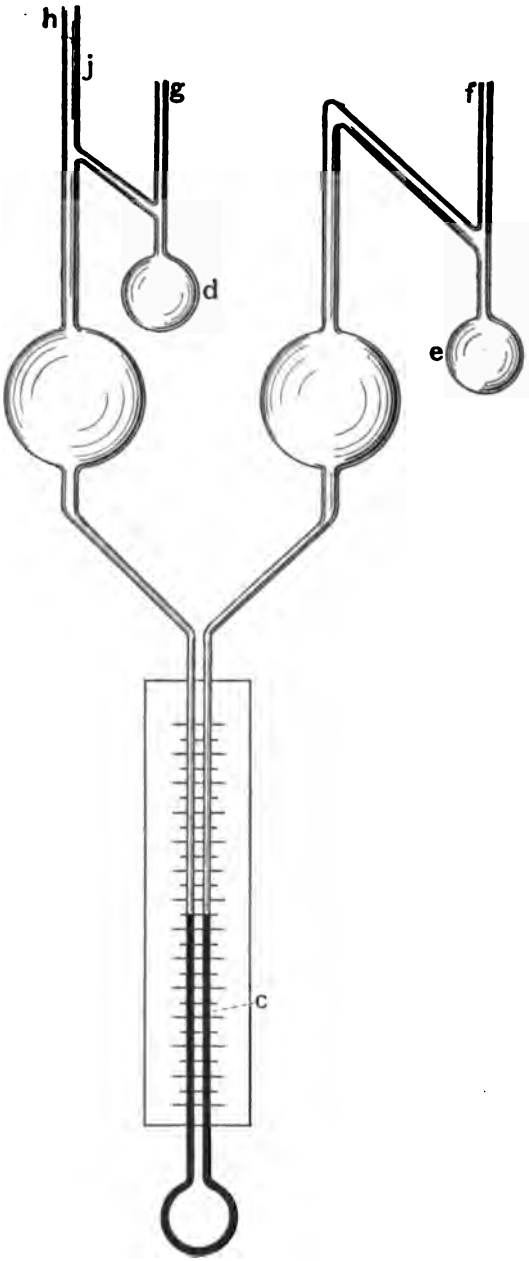

FIG. 1.

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employed in some cases to determine the transition point of the system. If we plot the solubility of each of the three substances (double salt and its two components) against the temperature through a given range, we shall obtain three curves which will cut each other in a point. This point gives the transition temperature.

It is a well-known fact that if we had two vessels containing solutions of some salt and connected together by a tube which allows the liquid to pass from one vessel to the other, we can obtain an electric current by immersing electrodes in the two vessels and connecting them by means of a wire. The current passes in the cell from the weaker to the stronger solution. Suppose that we take the case of the two hydrates of zinc sulphate, $ZnSO_4 . 7H_2O$ and $ZnSO_4 . 6H_2O$. We place saturated solutions of each of these in a vessel along with some solid salt, connect the two vessels with a tube bent in such a way as to prevent the action being disturbed by convection currents, and then dip into each vessel a zinc electrode. The electrodes are connected by a wire, and a galvanometer is included in the circuit. At temperatures below the transition point, the salt $ZnSO_4 . 6H_2O$ is more soluble than the other, so that the solution of the latter will be weaker in zinc sulphate. Hence the current will pass in the cell from the vessel containing the heptahydrate to that containing the hexahydrate. As we raise the temperature, the solubilities of the salts in the two vessels approximate more and more to each other, and consequently the current passing becomes weaker and weaker. Finally, at the transition temperature, it ceases to flow.

It has been shown[1] that the viscosity of a solution of a racemic compound is less than that of the corresponding active antipodes, and the transition temperature can be detected by the break in the temperature-viscosity curve.

4. Transition Intervals

We must next turn to examine the solubility relations which have been observed in the case of double salts and their components. We have already touched upon the matter in the last section when dealing with the determination of the

[1] Dunstan and Thole, *Trans.*, 1898, **93**, 1815.

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transition temperature by means of the solubility; but in the present section we must look upon the question from a somewhat different point of view.

It has been shown by van't Hoff and Müller[1] that the transition temperature of rubidium racemate is 40° C. Below this temperature the racemate exists; above it, the individual dextro- and lævo-tartrates. Now, suppose that we take equal weights of the dextro-tartrate and of the lævo-tartrate and place them both in a vessel containing the same weight of water at 15° C. Both tartrates will go into solution in equal quantity, since their solubilities are equal; and since there is not enough water present to dissolve them, part of each tartrate will remain as a solid phase. A complication now enters into the problem. As the tartrates go into solution they are converted into the corresponding racemate, which is the stable form below 40° C., and this racemate is less soluble than the tartrates. Consequently, the solution will be able to take up more of the single tartrates than it can keep in solution when they have combined to form a racemate. As a result we shall have a continual deposition of racemate to keep pace with the amount of tartrates taken up by the water. In this way we have first the solution of the two tartrates, then their conversion into racemate, and consequent supersaturation of the solution with racemate, leading to a deposition of crystals of the racemate; and this process will go on until all the tartrates have been dissolved.

This is a simple case, owing to the fact that the two components of the double salt have the same solubility; but we must consider a more complicated problem. Let us take the case of astrakanite, $MgSO_4 . Na_2SO_4 . 4H_2O$, as an example.[2] In this case the two components of the double salt have not the same solubility, and in the first place we have to find the solubility of the two component salts, sodium sulphate and magnesium sulphate, in presence of each other. This is done by placing an excess of both salts in contact with water and agitating at constant temperature until equilibrium is established, after which the solution is analyzed. In this way we obtain the following figures:—

[1] Van't Hoff and Müller, *Ber.*, 1898, **31**, 2206.
[2] See Findlay, *The Phase Rule*, 1906, p. 268.

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I.—Solid Phases: Sodium Sulphate and Magnesium Sulphate.

	Temperature.	Na_2SO_4.	$MgSO_4$.	Ratio of Na_2SO_4 to $MgSO_4$
A . . .	18·5°	21·6	45·7	1 : 2·1
B . . .	24·5°	34·3	46·8	1 : 1·4

The figures under Na_2SO_4 and $MgSO_4$ represent the number of molecules of the salt dissolved in a thousand molecules of water.

The transition point of astrakanite is about 22° C.: above this temperature the double salt exists; below it, the components are stable as independent salts. Let us examine what happens at the temperature 24·5°, which lies above the astrakanite transition temperature. At this temperature, as the figures above show, water will take up a greater number of molecules of magnesium sulphate than of sodium sulphate. But in solution these two salts will combine to form astrakanite, which is less soluble and will consequently crystallize out, just as the racemate did in the case of the rubidium salts. And since astrakanite contains magnesium and sodium sulphates in equimolecular proportions, it follows that at the end of the process we shall have an excess of sodium sulphate left as a solid phase, along with the other solid phase astrakanite. If we exclude the vapour phase, we have three phases present (solid astrakanite, solid sodium sulphate, and the solution); consequently the system is univariant, and at a given temperature the solution will have a definite composition.

If we take astrakanite and sodium sulphate in excess, place them in contact with water at a given temperature, and agitate the mixture until equilibrium is attained, we shall find that we obtain the following results[1] representing the number of molecules of magnesium and sodium sulphates dissolved in a thousand molecules of water:—

II.—Solid Phases: Astrakanite and Sodium Sulphate.

	Temperature.	Na_2SO_4.	$MgSO_4$.	Ratio of Na_2SO_4 to $MgSO_4$.
C . . .	22°	29·5	47·0	1 : 1·59
D . . .	24·5°	34·5	36·2	1 : 1·04
E . . .	30°	45·8	29·1	1 : 0·63

Repeating the process, but using in this case astrakanite and magnesium sulphate, we find the following results:—

[1] Roozeboom, *Zeitsch. physikal. Chem.*, 1888, **2**, 518.

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III.—Solid Phases: Astrakanite and Magnesium Sulphate.

	Temperature.	Na_2SO_4.	$MgSO_4$.	Ratio of Na_2SO_4 to $MgSO_4$.
F . . .	18·5°	34·1	42·7	1 : 1·3
C . . .	22°	28·5	46·8	1 : 1·6
G . . .	24·5°	26·8	47·6	1 : 1·8
H . . .	30°	28·0	53·1	1 : 2·8

Now let us fix our attention upon the temperature 24·5° C. If we take pure astrakanite and dissolve it in water at this temperature, we should get, in the first place, a solution containing exactly equimolecular quantities of sodium and magnesium sulphates. But if we look at Table II., under the temperature 24·5° C., we shall find that equilibrium is attained,

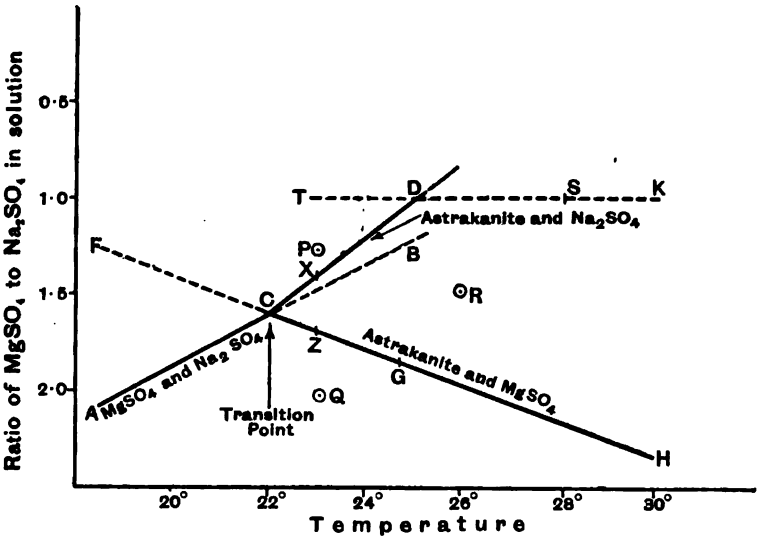

Fig. 2.

not when the two salts are present in exactly equivalent proportions, but when there is slightly less sodium sulphate present. Consequently, in order to reach the position of equilibrium, a solution of pure astrakanite must deposit some sodium sulphate. (We exclude the case of supersaturation for the sake of convenience.) Thus it will be impossible to obtain at 24·5° C. a solution of pure astrakanite.

Let us now construct from the data in the three tables given above a graphic representation of the relations between the various substances. The abscissæ in Fig. 2 represent the

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temperatures, while the ordinates show the ratio of magnesium to sodium sulphate in the various solutions. The diagram is only a rough one.

The line ACB represents solutions saturated with magnesium and sodium sulphates, and is drawn from the data in Table I. The line CD represents a series of solutions saturated with astrakanite and sodium sulphate, the data being taken from Table II. Similarly, the line CH is drawn from data in Table III., and represents a series of solutions in equilibrium with solid astrakanite and magnesium sulphate. If the experimental data were absolutely correct, these three lines would meet in the point C, which is the transition point of the system.

An examination of the figure will show that if we have a solution under conditions represented by the point P, it will contain more sodium sulphate than a saturated solution of magnesium and sodium sulphates or of sodium sulphate and astrakanite could do. It is therefore in a state of unstable equilibrium, and will begin to precipitate sodium sulphate. In other words, the line representing its change in composition will be PX, and the solution will come into equilibrium only when its composition can be represented by the point X, the temperature being kept constant throughout. Similarly, a solution represented by the point Q would contain an excess of magnesium sulphate, and part of this salt would separate out until the composition of the solution became representable by the point Z. Further, a solution represented by the point R would be unsaturated with regard to both sodium sulphate and magnesium sulphate.

We are now in a position to understand what happens when we dissolve pure astrakanite in water. Let us take the case of a solution at 28° C., which we can represent by the point S. All solutions of pure astrakanite in water will be represented by points on the line KSD, since all such points represent solutions containing equimolecular quantities of sodium and magnesium sulphates. Now, when we lower the temperature the composition of the astrakanite solution will remain unchanged until the point D is reached. At that point a change must take place, for if we attempt to continue along the line DT we shall produce a solution supersaturated with

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regard to sodium sulphate; hence precipitation will occur, and the solution will cease to contain the two sulphates in equimolecular quantities. The point D, then, marks the lowest temperature at which astrakanite can be dissolved in water without decomposition. But the lowest temperature at which astrakanite can exist is the transition point C. The interval between these two temperatures is called the *transition interval* for astrakanite solutions.

5. The Existence of Double Salts in Solution

When we mix solutions of two salts containing a common ion, it may in some cases be important to know whether the solution contains a mixture of the two original salts or a new double salt. Various methods have been suggested for ascertaining this, some of them being adaptations of those employed in the determination of transition temperatures. It is obvious that physical methods alone can be employed, as chemical experiments can tell us nothing in the matter, unless we are able to isolate the solid substances and analyze them with a view to finding differences in the amount of water of crystallization or some such property.

In applying physical methods to the problem, we begin with the most obvious property, colour. Many cases are known in which the formation of a double salt produces an absorption spectrum different from that of the components. We have already quoted the case of the double salt of potassium and ferric chlorides, whose formation gives rise to a red tint in the previously yellow solution. When we mix a solution of colourless lithium chloride with one of green cupric chloride, we obtain a garnet-coloured double salt. Other instances might be quoted.

Conductivity measurements[1] may also be employed to test whether or not a double salt is present in solution. We can calculate the conductivity of a mixture of two salts in solution; and it has been found in many cases that if we use fairly strong solutions the observed conductivity differs to a considerable

[1] Archibald, *Trans. Nov. Scot. Inst. Sci.*, 1891, **9**, 307; Jones and his collaborators, *Amer. Chem. J.*, 1897, **19**, 83; 1899, **22**, 5; 1900, **25**, 349; Lindsay, *ibid.*, 1901, **25**, 62.

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extent from the calculated value, thus showing that double salt formation has taken place.

Magnetic rotation[1] has been used in a similar manner. The values for two separate substances are first obtained, and the rotation due to a mixture of them is calculated in the usual way from the mixture rule. The actual value found by experiment will differ from the calculated one, if any interaction between the salts occurs.

The depression of the freezing-point of solutions has also been of service in this field. We first ascertain the depression produced by given quantities of the two components, and then calculate their joint effect upon the freezing-point. If this corresponds to the experimental results obtained with a solution containing a mixture of the two components, no double salt formation has taken place at that temperature. If the calculated and experimental values do not agree, a double salt has been formed.

6. Criteria of the Nature of Equimolecular Mixtures of Optical Antipodes

The last problem in connection with double salts which we need enter into is that of the nature of the crystals which are produced when equimolecular quantities of two optical antipodes crystallize from a solution together. It is obvious that in this case we may have one of three possibilities: the substances may form a true double salt; they may successively crystallize in separate layers round the same nucleus, producing a mixed crystal; or, finally, they may simply crystallize out of the solution as a conglomerate, a mixture of crystals of each separate antipode.

It is well known that the melting-point of a substance is lowered by the solution in it of a foreign substance. For example, the melting-point of water is very considerably lowered when salt is added to the liquid. Now, the same rule will hold even if the relative amount of the solvent be decreased; and, consequently, if we increase the amount of solute and diminish the amount of solvent, we shall eventually reach a minimum value for the melting-point of the mixture.

[1] Schönrock, *Zeitsch. physikal. Chem.*, 1898, 11, 776.

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If the process be continued, it is clear that eventually the solvent will be present in less quantity than the solute, so that their relative positions are altered: what was at first the solvent now becomes the solute. When this point has been passed, the melting-point of a mixture of the two bodies will rise rather than fall, for the proportion of solvent to solute is now steadily increasing.

Let us apply this to the case of two optical antipodes. Suppose that they do not combine with each other chemically; in that case we may have a conglomerate or a mixed crystal present in the solid condition.

If A (Fig. 3) represents the melting-point of, say, the dextro form, then as some of the lævo variety is gradually added to the pure dextro form, the melting-point of the mixture will gradually fall until it reaches a minimum at C, when equal quantities of the dextro and lævo forms are present in the mixture. Now, let F represent the melting-point of the lævo form. Since the melting-points of optical antipodes are identical, DF will be equal to BA. As we add more and more of the dextro form to the lævo substance, the melting-point of the mixture will fall just as the last case, and in the end it will be represented by the point C. It is evident that at C both antipodes will be present in equal proportions. Hence, if we add to such a mixture as this a small quantity of either antipode, the melting-point of the new mixture will be *higher* than that of the equimolecular mixture.

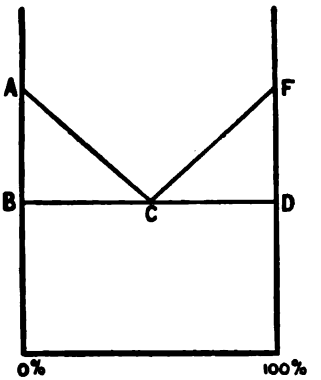

FIG. 3.

In the case of a mixed crystal composed of two optical antipodes, there are various possible forms for the curve representing the melting-points of a set of mixtures of different composition. Of these possible curves, only two have been as yet observed in practice. They are of the forms shown in Figs. 4 and 5.

It has been found that the oximes of dextro- and lævo-camphor, for instance, form a series of mixed crystals, all of

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which have the same melting-point. The curve of the melting-points of these mixtures is therefore a straight line An example of the other form of curve is furnished by the carvoximes. In this case a maximum is found, as shown in the figure.

With regard to racemic substances, we have an actual compound present. Consequently, since we are now dealing with three substances (the two antipodes and the racemic compound), we shall have two sets of curves, one showing the relations between the dextro antipode and the racemic substance, the

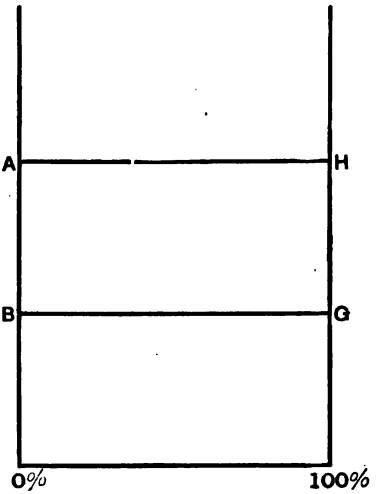

FIG. 4.

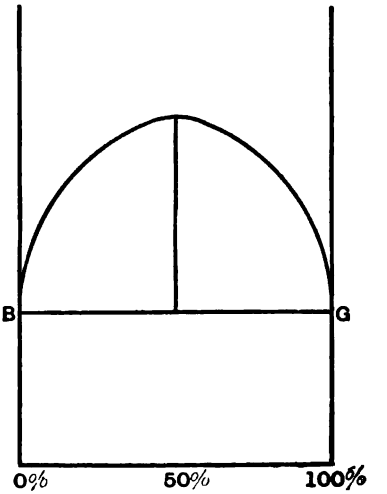

FIG. 5.

other illustrating those between the racemic compound and the lævo isomer. Figs. 6 and 7 show possible forms of the curves. This case is really a repetition of the one we first dealt with, but here the figure is repeated twice over. If the racemic compound be considered as taking the place of one of the antipodes, A represents the melting-point of the dextro form, H that of the lævo isomer, and D that of the racemate. The abscissæ along BK represent graphically the percentages of dextro isomer and racemic compound present; while those along KG represent the percentages of racemate and lævo antipode. It can be seen that an addition of either the dextro

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or the lævo form to the racemate will result in a lowering of the melting-point.

We are now in a position to understand the method to be applied. We have before us an optically inactive crystalline body which is made up of equal quantities of dextro and lævo forms; and we have to decide whether it is a conglomerate, a mixed crystal, or a racemate. We take its melting-point. Then we add to it a small quantity of one of the antipodes, and take the melting-point of the mixture. We continue this process, adding each time rather more of the antipode than we used in the previous experiment. In this way we are able to

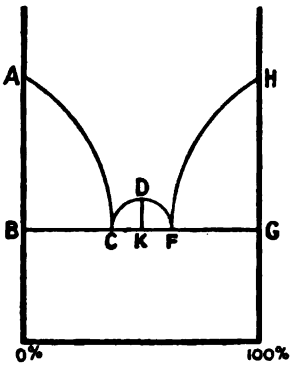

FIG. 6.

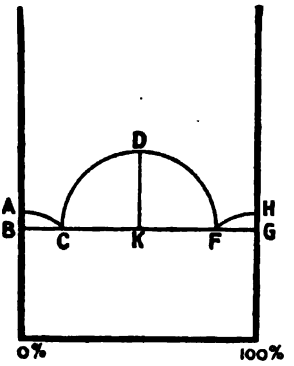

FIG. 7.

plot the curve of the melting-points of the mixtures. If this curve is a straight line parallel to the X axis, or if it is a curve of the type shown in Fig. 5, then we have a mixed crystal. If, on the other hand, we get first a fall in the melting-point, and then a rise as we increase the quantity of antipode in our mixture, it is obvious that we are dealing with a true racemic compound, for the curve will resemble one of those shown in Figs. 6 and 7. Finally, if the addition of more and more antipode to the inactive body produces a series of mixtures whose melting-points are higher and higher, then we evidently have merely a conglomerate before us, and the curve will be one of the branches of that shown in Fig. 3.

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CHAPTER II

THE PROBLEM OF THE OCEANIC SALT DEPOSITS

1. The Stassfurt Salts

In various parts of the earth, large tracts of sedimentary deposits have been discovered which contain very high percentages of common salt. Such strata form the most valuable source of salt at the present day; but in addition to their practical value, they offer a further claim to attention on account of some physico-chemical questions which their existence suggests. The most important deposit is to be found at Stassfurt, and we may describe its characteristics briefly before entering into a discussion of these problems.

The salt strata in the Stassfurt district may be divided into four types. Beginning at the top, we have a layer of carnallite ($MgCl_2 . KCl . 6H_2O$) mixed with a little rock salt; this bed may be anything up to thirty metres in depth. Below this comes a stratum of rather greater thickness made up of kieserite ($MgSO_4 . H_2O$): the percentage of rock salt in this layer is rather greater than in the carnallite bed. Deeper still we come to a zone in which the prevailing mineral is polyhalite ($MgSO_4 . K_2SO_4 . 2CaSO_4 . 2H_2O$); while the fourth stratum is chiefly made up of anhydrite ($CaSO_4$). The polyhalite and anhydrite regions are remarkable for the manner in which the characteristic minerals are interspersed with regular layers of rock salt: first comes a layer of rock salt; then a layer of polyhalite, then another layer of rock salt, and again a layer of polyhalite. Below the anhydrite strata lies the main bulk of the common salt deposits. Fig. 8 shows an ideal section of these strata.

While the problem of the conditions under which the Stassfurt beds were laid down is most important from the

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point of view of geology, it is evident that very little progress could be made towards its solution by the means at the disposal of geologists. Apart from the suggestion that the alternating layers of salt and polyhalite, etc., owed their origin to the change of temperature with the seasons, there seemed little chance of any results of value being obtained. In the hands of van't Hoff and his collaborators, however, the whole question has been opened up and developed to such a point

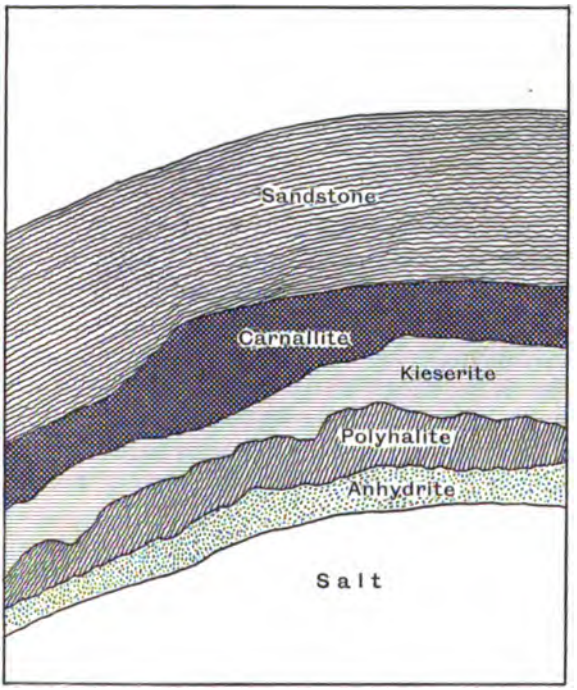

FIG. 8.

that we can now tell even the temperature of the period at which any particular series of beds were deposited. In the following pages a brief account of these researches will be given.

2. THE RESEARCHES OF USIGLIO AND OF VAN'T HOFF

From the composition of the Stassfurt deposits, it seems probable that they were originally formed by the evaporation

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of sea-water; and hence it may at first sight appear perfectly simple to repeat the process in the laboratory by evaporating sea-water to dryness. This was carried out on a large scale by Usiglio;[1] but the results obtained by him failed to correspond with the natural deposits in several important respects. For example, he obtained neither kieserite, polyhalite, nor anhydrite, though these substances are the predominant factors in the middle strata at Stassfurt.

Several causes probably contributed to the failure of Usiglio's experiments. In the first place, at the time when he carried out his work, the question of transition temperatures had not been thoroughly investigated, and consequently this important factor was perforce left out of the calculation. This alone would have made success very doubtful in the case of the deposition of double salts, but there were many other drawbacks to his method. In artificial experiments, even on the largest scale, there are many sources of error which prevent the action from proceeding on lines exactly parallel to those followed by the natural process. There may be supersaturation in a small tank; the layers of two deposits may be so intimately mixed that it is difficult to determine which came down first; or, again, after one solute has separated out from the solution its crystals may become crusted over with layers of a second solute, so that there may be no solid phase of the first solute in contact with the solution.

It is therefore evident that, in order to obtain an insight into the conditions under which the Stassfurt strata were laid down, we must have recourse to methods more refined than the mere evaporation of sea-water. The question remained practically at this stage until the year 1887, when van't Hoff[2] and his collaborators attacked the problem from a different point of view.

Instead of taking a solution like sea-water, which contains a very large series of solutes, van't Hoff in his researches worked from simple to more complex cases. The simplest case is, of course, that in which there is only a single solvent and a single solute. In such an instance, evaporation would

[1] Usiglio, *Ann. chim. phys.* (iii.), 1849, **27**, 92, 172.

[2] Van't Hoff, *Zur Bildung der ozeanischen Salzablagerungen*, vol. i. (1905), vol. ii. (1909).

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proceed until the solvent was saturated with the solute, after which, if more solvent evaporated, the solute would begin to separate out from the mother-liquor. The case of two or more solutes is more complicated, and we must devote another section to its consideration.

3. Solutions of Potassium and Sodium Chlorides

If we dissolve two salts, such as sodium chloride and magnesium sulphate, in water, it is evident that we shall at once have a double decomposition taking place, so that if we were to evaporate the solution we should obtain a mixture of magnesium sulphate, magnesium chloride, sodium chloride, and sodium sulphate. The original two salts would give rise to two new salts, thus complicating the problem very considerably. It becomes clear, therefore, that if we are to deal with a case which does not involve these complications, we must restrict ourselves to two salts having a common ion, such as two chlorides or two potassium salts. Further, we must be careful to select two salts which do not combine together to yield a double compound, as this would confuse the matter to some extent.

We may choose, as a concrete example, the case of potassium chloride and sodium chloride; and we may take the temperature at the time of the experiment as 25° C. Under these conditions, a saturated solution of sodium chloride contains one hundred and eleven molecules of salt in a thousand molecules of water. Under the same conditions, a saturated solution of potassium chloride contains eighty-eight molecules of salt in a thousand molecules of water.

Now, suppose we take a saturated solution of sodium chloride and add to it potassium chloride, two results will follow. In the first place, potassium chloride will be dissolved; but as more and more is added it will finally be present in greater quantity than the solution can take up, and further addition of it will have no effect. The solution which we thus obtain is saturated with respect to both potassium chloride and to sodium chloride. It is termed a *constant solution*, and is composed of—

Potassium chloride	89	molecules
Sodium chloride	89	,,
Water	1000	,,

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We must now attempt to express these relations graphically (see Fig. 9). We take two rectangular axes, OX and OY, and let distances measured along OY represent the number of molecules of potassium chloride in a thousand molecules of water, while distances along OX represent the analogous measurements for sodium chloride. Then P will indicate the saturation point of the solution with regard to potassium chloride, since OP is eighty-eight units in length. Further, R represents the saturation point of a solution of sodium chloride in water, OR being a hundred and eleven units in length. The co-ordinates of the point Q are, of course, thirty-nine along OY, and eighty-nine along OX.

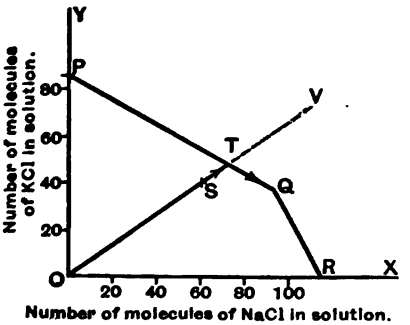

FIG. 9.

A consideration of the figure will show that the composition of any possible solution of sodium chloride and potassium chloride can be represented by some point inside the figure OPQR. Further, points outside OPQR represent merely ideal solutions; for in practice any attempt to add to the solution more salt than can be represented by a point within the figure would result merely in the deposition of a corresponding amount of salt.

Let us next consider the case of some definite solution, and see if we can foretell its behaviour on evaporation. Suppose we take as an example a solution containing forty molecules of potassium chloride and sixty of sodium chloride in a thousand molecules of water. To obtain the point corresponding to this composition, we measure sixty units along OY and forty units along OX, and in this way we find the point S. When we begin to evaporate this solution, it is evident that at first we do not alter the ratio of potassium to sodium chloride contained in it; we merely remove the water. The solution therefore becomes more concentrated, while at the same time the ordinate and the abscissa of the point representing it maintain the same ratio to each other as before. Now, the

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ordinate of any point on OV is obviously two-thirds of the corresponding abscissa; and the line OV represents a series of solutions in which the ratio of sodium to potassium chloride remains always the same, though the proportion of water present decreases as the distance from O increases.

As we evaporate the solution, then, the point representing its composition will move from S along OV in the direction of V. When it reaches the point T we have a solution which is saturated with potassium chloride, and consequently some of that salt will separate out. If the evaporation be continued, it is obvious that the point representing the solution's composition cannot move along the dotted line TV, as no such solution can exist; experiment shows that it moves as shown by the arrow, in the direction of Q. When, by further evaporation, the composition of the solution becomes that which is represented by the point Q, no further change takes place; the two solutes are then present in such proportions that their rates of crystallization are exactly proportional to the quantity of each substance which is present in solution. The solution therefore yields crystals of a constant composition and goes down to dryness without change in concentration. The point Q is termed the *end-point of crystallization.*

These results van't Hoff[1] summarizes in the following rule: "A solution in depositing a solute changes its composition *away from* that of a saturated solution of this solute alone."

4. The Case of Carnallite

In the foregoing section we examined the case of a solution containing two non-combining solutes; in the present section we must take up a slightly more complicated case. When we mix together under certain conditions of temperature solutions of magnesium and potassium chlorides, a double salt called carnallite is formed, which has the composition—

$$MgCl_2 . KCl . 6H_2O$$

It is evident that the formation of this body differentiates the case of a solution of magnesium and potassium chlorides from the solution of sodium and potassium chlorides with which

[1] Van't Hoff, *Oceanischen Salzablagerungen*, i. p. 12.

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we have dealt. Instead of two solutes we have now three: magnesium chloride, potassium chloride, and carnallite. Thus we have to determine the solubility relations of—

1. Potassium chloride in water.
2. Magnesium chloride in water.
3. Carnallite in magnesium chloride solution.
4. Carnallite in potassium chloride solution.

As in the last case, we take two rectangular axes, along one of which we measure the number of molecules of potassium chloride in a thousand molecules of water, while along the

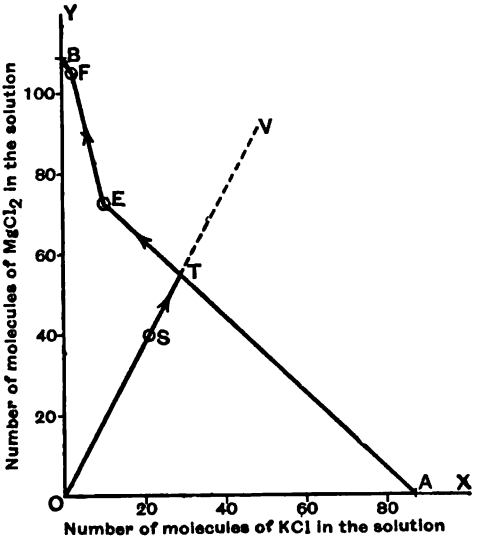

FIG. 10.

other we measure the number of molecules of magnesium chloride in the same quantity of water. The point A (see Fig. 10) represents a saturated solution of potassium chloride (88 KCl in 1000 molecules H_2O). The point B represents a saturated solution of magnesium chloride (108 molecules $MgCl_2$ in 1000 H_2O).

Now, suppose we take the saturated potassium chloride solution represented by the point A and add to it some magnesium chloride. The two salts at once combine to form carnallite. Consequently the solution is really one containing carnallite and potassium chloride; so that by the continual

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addition of magnesium chloride we are really approaching a constant solution of carnallite and potassium chloride instead of a constant solution of magnesium and potassium chlorides. This constant solution is obtained when we have present—

Potassium chloride	11 molecules.
Magnesium chloride	72·5 ,,
Water	1000 ,,

This point is represented on the figure by the point E.

If we begin with a saturated solution of magnesium chloride and add to it potassium chloride, a similar process takes place. The added potassium chloride combines with the excess of magnesium chloride, forming carnallite again; but in this case the constant solution formed by continued addition of potassium chloride is one containing carnallite and magnesium chloride and having the composition—

Potassium chloride	2 molecules.
Magnesium chloride	105 ,,
Water	1000 ,,

In the figure this is represented by the point F.

If, as in the previous section, we take the case of a solution of the composition shown by the point S, we can now tell exactly what will happen when it is evaporated. In the first place, water will be driven off, and the point S will move along OV towards V until it reaches T, beyond which it cannot go. At this point there is an excess of potassium chloride in the solution, and as the concentration increases it is found that this separates out. That is to say, the point representing the solution will move from T along TE towards E.

At this point there are two possible courses open. If we remove from the vessel all the solid potassium chloride which separates out from the solution, the composition of the solution will follow the line EF, becoming richer in magnesium chloride. In this case, F is the end-point of crystallization. On the other hand, if we do not remove the solid potassium chloride from the solution, it is attacked by the magnesium chloride with the formation of carnallite, which then crystallizes out. In this case the composition of the solution remains constant, and a continuous separation of carnallite takes place.

Of course in this, as in the previous figure, the lines should

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not be quite straight, but the deviation from straightness is probably not great.

5. The Case of the Chlorides and Sulphates of Magnesium and Potassium

We must now proceed to examine a still more complicated case, in which the number of possible constant solutions increases greatly. If to a solution of potassium chloride we add magnesium sulphate, we obtain in the consequent double decomposition a solution which contains four salts: potassium chloride, potassium sulphate, magnesium chloride, and magnesium sulphate. As we shall find later, it contains other salts as well; but for the present we may confine our attention to these.

As in the last case, we must determine the solubility of each of the four salts in water. The number of molecules of each salt which can be dissolved in a thousand molecules of water is given in the following table:—[1]

A.	K_2Cl_2	44 molecules *
B.	$MgCl_2$	108 ,,
C.	$MgSO_4.7H_2O$	55 ,,
D.	K_2SO_4	12 ,,

To this table we have to add a second showing the relations between carnallite and its components—

		Molecules of K_2Cl_2	Molecules of $MgCl_2$ saturate 1000 H_2O
E.	K_2Cl_2 and carnallite	5·5	72·5
F.	$MgCl_2$ and carnallite	1	105

Then we have to take into account the relations of magnesium chloride to the two hydrates of magnesium sulphate, as well as the reciprocal relations of the two latter bodies. These are expressed in the following figures:—

		Molecules of $MgCl_2$	Molecules of $MgSO_4$ saturate 1000 H_2O
G.	$MgCl_2$ and $MgSO_4.6H_2O$	104	14
H.	$MgCl_2$, $MgSO_4.7H_2O$ and $MgSO_4.6H_2O$	73	15

[1] For these and the following figures and diagrams, van't Hoff's *Oceanischen Salzablagerungen* has been utilized.

* Van't Hoff reckons potassium chloride in terms of double molecules in order to bring it into line with the other salts.

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The formation of $MgSO_4 . 6H_2O$ is due to the dehydrating action of the magnesium chloride; so that the hexahydrate is formed only in solutions containing that substance.

When the sulphates of magnesium and potassium occur in the same solution, there is a possibility of the formation of the double salt schönite, $MgSO_4 . K_2SO_4 . 6H_2O$, so that this in turn must be taken into account. We therefore obtain two more sets of data—one showing the relation of magnesium sulphate to schönite; the other giving the relation of schönite to potassium sulphate—

	Molecules of $MgSO_4$	K_2SO_4 in 1000 mols. H_2O
I. $MgSO_4.7H_2O$ and schönite .	58·5	5·5
K. K_2SO_4 and schönite . . .	22	16

To complete the series, we now require to know the relations between potassium sulphate and potassium chloride. These are given in the following figures :—

	Molecules of K_2Cl_2	K_2SO_4 in 1000 mols. H_2O
L. K_2SO_4 and K_2Cl_2 . . .	42	1·5

In the foregoing data we have taken each substance separately; then we have taken their double salts; and finally we have taken them in pairs. We must next take the data found when the substances are present three at a time. These data are given in the table below :—

	Molecules of K_2Cl_2	$MgCl_2$	$MgSO_4$ in 1000 mols. H_2O
M. K_2Cl_2, K_2SO_4, schönite . .	15	21	11
N. K_2Cl_2, $MgSO_4.7H_2O$, schönite .	9	55	16
P. K_2Cl_2, $MgSO_4.7H_2O$, $MgSO_4.6H_2O$	8	62	15
Q. K_2Cl_2, carnallite, $MgSO_4.6H_2O$.	4·5	70	18·5
R. $MgCl_2$, carnallite, $MgSO_4.6H_2O$	2	99	12

These figures complete the data required, and we must now proceed to express them graphically. For this purpose van't Hoff chose rectangular axes as in the previous cases, and carried out the construction of his figure in the following manner (see Fig. 11). Along the axis OA he measured off forty-four units, corresponding to the quantity of potassium chloride required to saturate a solution. Similarly the point B represents the saturation point of a solution of magnesium chloride, point C represents a saturated solution of magnesium sulphate, and D a solution saturated with potassium sulphate.

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The positions corresponding to the constant solutions are then filled in as before at E, F, G, H, K, and L.

The diagram which we thus obtain is not satisfactory,

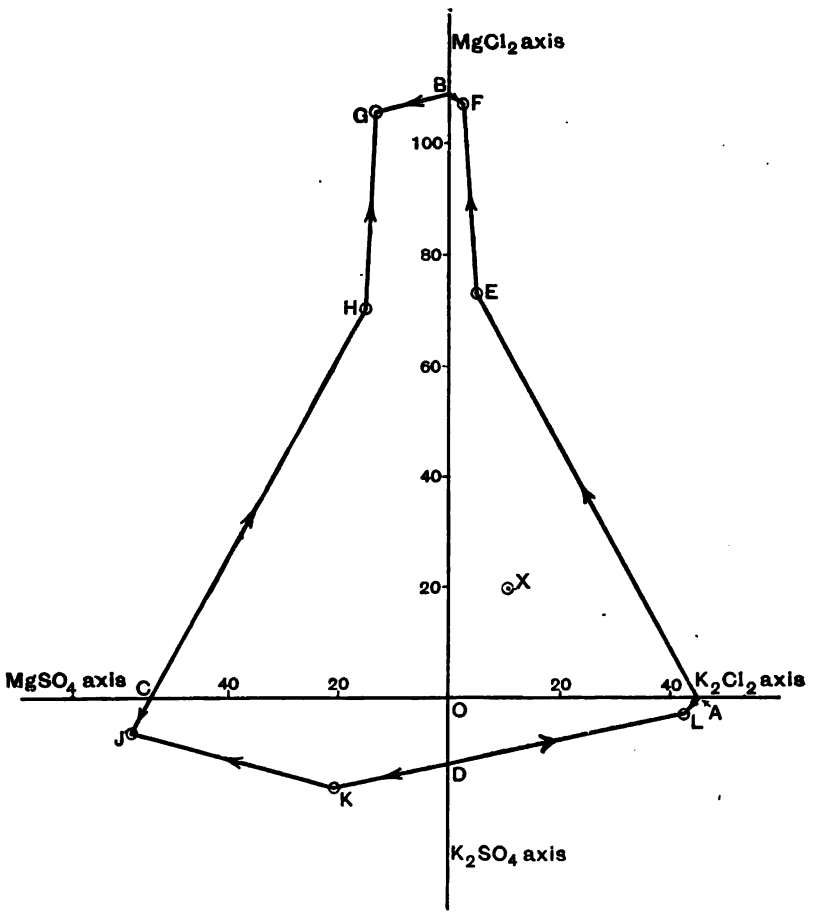

FIG. 11.

however, as the following consideration shows. Let us take the concrete case of two solutions, one of which (I.) contains

10 molecules K_2Cl_2
20 molecules $MgCl_2$
0 molecules $MgSO_4$

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while the other (II.) contains

30 molecules K_2Cl_2
20 molecules $MgCl_2$
20 molecules $MgSO_4$

If we attempt to insert these in the plane figure (Fig. 11) we must for case (I.) measure from O ten units along OA, then turn at right angles and measure twenty units parallel to the direction OB. This will place us at the point X, which should thus represent the composition of the solution I. In the case of solution II., we start again from O, measure thirty units towards A to represent the quantity of K_2Cl_2 present; then in the reverse direction—towards C—measure twenty units to represent the amount of $MgSO_4$ in the solution. This leaves us at a point ten units from O in the direction OA. We then measure from this point twenty units up the paper in the direction OB, and this brings us in this case also to the point X. Thus two solutions would be represented by the same point X.

In order to avoid such confusion, van't Hoff inserted another co-ordinate into his scheme. From every point in the plane of the paper he raises a perpendicular whose length is proportional to the number of molecules of all kinds which are present in the solution. For example, in the two cases given above, a perpendicular would be raised from the point X; on this perpendicular we should cut off a distance of thirty units (10 molecules K_2Cl_2 + 20 molecules $MgCl_2$ = 30 molecules in all), and the point thus obtained would represent solution (I.). Since solution II. contains seventy molecules, we should have to travel seventy units up the perpendicular from X before we arrived at the point which represents its composition.

When we have in this way filled in the five points corresponding to the solutions M, N, P, Q, and R, we shall have the outline of a space-model whose appearance is shown in the perspective sketch, Fig. 12. Each face of this model represents a solution saturated with the salt whose name is placed upon it in the figure.

We must now endeavour to see how this model can be utilized. As far as the edges are concerned, there is no difficulty; the lines AE, BF, etc., have exactly the same

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meaning as the lines in Figs. 2, 3, and 4; and the route followed in crystallization can be foretold by the van't Hoff rule just as in the previous cases. The arrows in the figure indicate this.

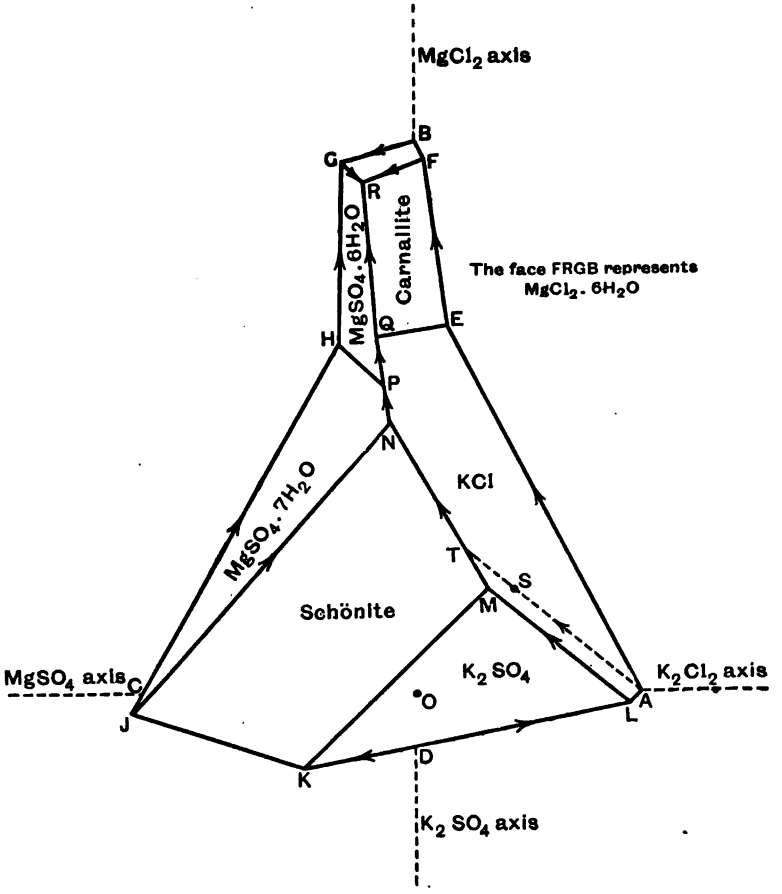

FIG. 12.

The case is not much more complicated if we start from a solution whose composition is represented by a point on one of the faces. Suppose we take the point S in Fig. 12. This point lies on the potassium chloride face, so that an evaporation of the solution will cause the separation of that salt. Since the point A represents a saturated solution of potassium

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chloride, we join S to A. Then according to the van't Hoff rule, the point representing the composition of the solution will pass (as the solution is evaporated) along AS produced away from A. It will thus cut the edge MN in T, and thereafter the crystallization process will follow the direction of the arrows as shown.

We need not enter in detail into cases in which the point representing the composition of the original solution lies inside the surface of the space model; it is, of course, more complicated, but the same rules apply there also.

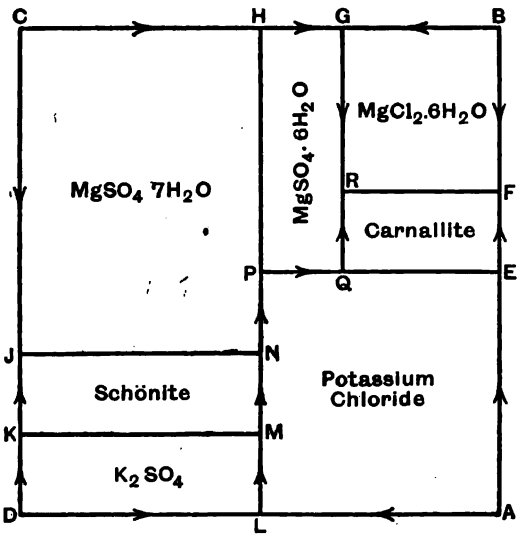

FIG. 13.

Since the space model is somewhat clumsy, we may replace it in a way by a simplified figure which gives equally well the relations between the various faces (see Fig. 13).

6. THE CASE OF FIVE SALTS

If to the salts dealt with in the last section we add sodium chloride, we shall obtain a solution which closely corresponds to that from which the upper bed of Stassfurt must have been laid down. The case is an extremely complicated one, there being no fewer than twenty-six different possible solutions

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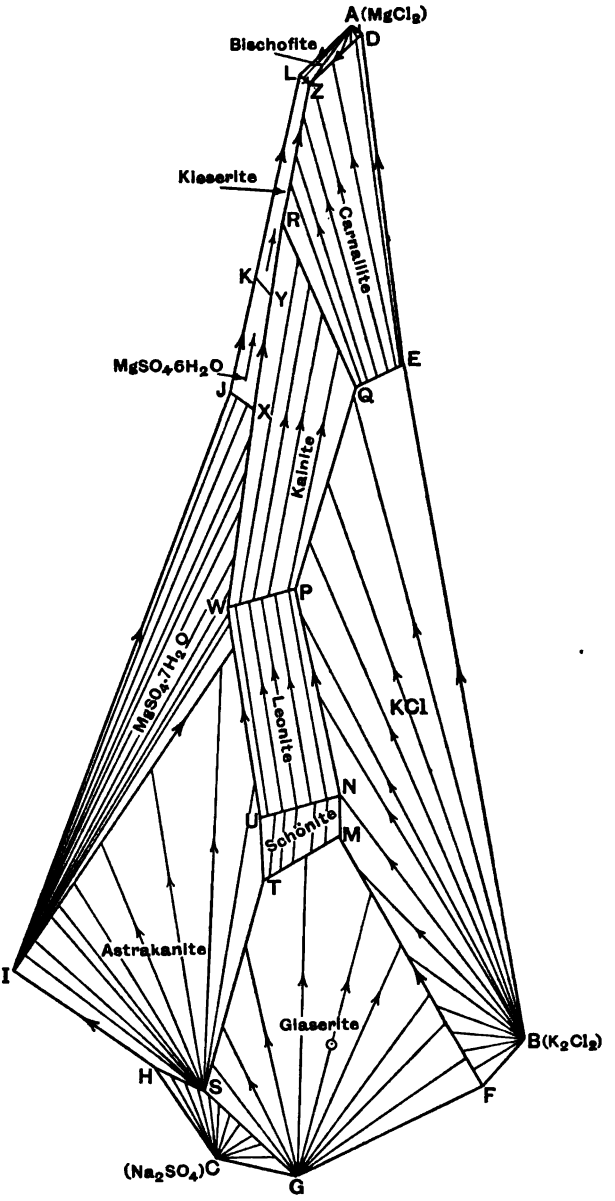

FIG. 14.

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and combinations of solutes to be taken into account. We

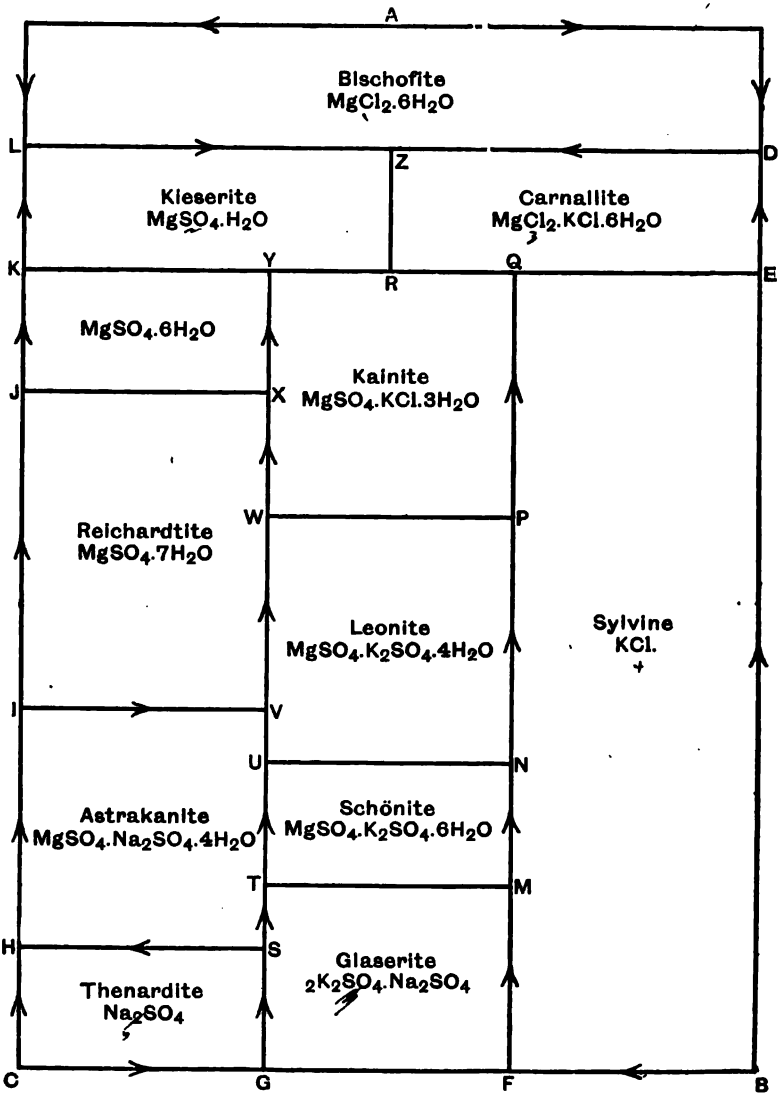

FIG. 15.

may content ourselves with reproducing van't Hoff's sketch of the space model (Fig. 14) as well as the plane arrangement

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derived from it (Fig. 15). This model corresponds to a set of experiments carried out at a temperature of 25° C.

7. The Influence of Time

At this point we must deal with another factor in the question which complicates matters very considerably. In the course of his earlier researches, van't Hoff found that in many of the solutions employed by him supersaturation occurred, with the result that salts which should theoretically have appeared at a certain stage of the evaporation process did not begin to crystallize from the solution until much later. The salts which thus appeared in the wrong place were kieserite ($MgSO_4 . H_2O$), leonite ($MgK_2(SO_4)_2 . 4H_2O$), and kainite ($MgSO_4 . KCl . 3H_2O$) Van't Hoff, in order to detect the presence of these bodies, brought into action the differential tensimeter. The salts which now and then fail to crystallize at the points where they are expected are all dehydration products of salts already present in solution: they must therefore be formed in a solution whose tension is smaller than that of the water of crystallization in the undehydrated salts. By means of the differential tensimeter, we can decide which form will appear.

For example, at 25° C., the tension of the water of crystallization of magnesium sulphate hexahydrate is greater than the tension of a solution containing magnesium sulphate hexahydrate, carnallite, and magnesium chloride; and it is therefore to be expected that when the hexahydrate is brought into contact with the solution, it will be dehydrated. This actually occurs in practice, and can be detected by means of the tensimeter. Again, at 25° C. a saturated solution of schönite may be supersaturated with leonite, which contains two molecules less water of crystallization; so that this salt must be taken into account when the examination of the solution is made.

These supersaturation questions naturally complicate the problem very much, for they result in crystallization hanging fire to a greater or less extent, and thus creating a discrepancy between theory and practice.

There appears to be some relation between the retardation

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of crystallization and a number which is called the *mean valency* of compounds. This mean valency is obtained in the following manner. As a numerator we take the sum of the number of valencies of the ions into which the salt dissociates in solution, and add four units for each molecule of water of crystallization. The denominator of the fraction is obtained by adding together the number of ions and three units for each molecule of water of crystallization.

A few examples will make the matter clearer.

Gypsum, $CaSO_4 . 2H_2O$	$\frac{2+2+8}{1+1+6} = 1{\cdot}5$
Glauberite, $CaNa_2(SO_4)_2$	$\frac{2+2+4}{1+2+2} = 1{\cdot}6$
Colemanite, $Ca_2B_6O_{11} . 5H_2O$ . .	$\frac{4+18+20}{2+6+15} = 1{\cdot}83$
Ascherite, $MgBO_2H$	$\frac{2+3+1}{1+1+1} = 2{\cdot}0$

In this series of substances, there will be less retardation in the crystallization of gypsum than in that of glauberite, while ascherite will show the greatest resistance to crystal formation.

8. Paragenesis and the Influence of Temperature

An examination of Fig. 15 will show that some of the rectangles are conterminous, while others do not touch each other. For example, the rectangles representing kainite and schönite do not touch each other in any point; while the rectangle denoting sylvine touches those symbolizing kainite, leonite, schönite, and glaserite. This indicates, as has been shown experimentally to be the case, that while sylvine can co-exist in solution with kainite at 25° C., astrakanite cannot do so. But if two substances cannot co-exist in solution it is evident that they cannot occur together in the same salt stratum; for their occurrence together would show that they had crystallized out side by side from the solution. Hence our space model can be made to serve another purpose, viz., to tell us whether or not we can expect to find two minerals occurring in the same mineral layer. Further, if we do discover cases in which astrakanite and kainite occur in the same stratum, then we can at once say that the temperature at the time of deposition could not have been 25° C.

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This question of *parageneses*, as van't Hoff called it, led him to take up an elaborate series of supplementary researches, in the course of which he determined, in the presence of sodium chloride, the transition temperatures of all the double salts shown in the following table:—

Mineral.	Composition.	Existence-limits.	
		Upper.	Lower.
Thenardite	Na_2SO_4	—	18·5
Glauber salt	$Na_2SO_4.10H_2O$	18	—
Kieserite	$MgSO_4.H_2O$	—	18
Schönite	$MgSO_4.K_2SO_4.6H_2O$	26	—
Reichardtite	$MgSO_4.7H_2O$	31	—
Hexahydrate	$MgSO_4.6H_2O$	85·5	18
Langbeinite	$K_2SO_4.2MgSO_4$	—	37
Loewite	$2MgSO_4.2Na_2SO_4.5H_2O$	—	43
Vanthoffite	$MgSO_4.3Na_2SO_4.4H_2O$	—	46
Astrakanite	$MgSO_4.Na_2SO_4.4H_2O$	60	4·5
Leonite	$MgSO_4.K_2SO_4.4H_2O$	61·5	18
Kainite	$MgSO_4.KCl.3H_2O$	83	—

These data furnish us with the means of foretelling the outlines of the crystallization process which will take place when a solution containing these salts is evaporated. Let us choose the temperature 84° C. as a starting-point. At that temperature, the only double salts which can exist are carnallite, langbeinite, glaserite, vanthoffite, and loewite; but crystals of bischofite ($MgCl_2$), kieserite ($MgSO_4 . H_2O$), thenardite (Na_2SO_4), and sylvine (KCl) may also be formed.

When the liquid cools down one degree, kainite ($MgSO_4.KCl . 3H_2O$) makes its appearance, as it has then reached its upper existence limit, 83° C. The solution will go on depositing these ten minerals until the temperature falls to 61·5° C., at which point leonite ($MgSO_4 . K_2SO_4 . 4H_2O$) first occurs. One and a half degrees lower, astrakanite ($MgSO_4 . Na_2SO_4.4H_2O$) begins to be formed. The temperature must now fall to 46° C. before further change takes place; but at this point we reach the lower limit for the existence of vanthoffite ($MgSO_4 . 3Na_2SO_4 . 4H_2O$), and it consequently ceases to be deposited from the solution. After the temperature reaches 43° C., loewite ($2MgSO_4 . 2Na_2SO_4 . 5H_2O$) in turn disappears; and at 37° C. langbeinite ($2MgSO_4 . K_2SO_4$) also ceases to

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crystallize out. At 35·5° C. it becomes possible for the hexahydrate of magnesium sulphate to be deposited; at 31° C. the heptahydrate, reichardtite, appears, and at 26° C. we begin to find deposits of schönite ($MgSO_4 . K_2SO_4 . 6H_2O$).

When the temperature reaches 18° C., three simultaneous changes occur; for on the one hand we reach the upper limit of existence of Glauber's salt, which therefore makes its appearance, while on the other hand we find that both kieserite and leonite disappear at this point.

At 13·5° C., thenardite (Na_2SO_4) disappears, the Glauber salt taking its place. Then, if the temperature falls half a degree, we reach the lower limit of existence of the hexahydrate of magnesium sulphate. Finally, at 4·5° C. astrakanite ceases to exist.

Data such as these, however, only allow us to judge roughly the temperature which must have existed when a certain bed was laid down. A much more accurate method of determining this temperature is to be found in the state of paragenesis which is observed in the strata in question. We cannot go into the matter in detail; but an examination of the annexed table,[1] and of Figs. 16 and 17, will show the applicability of the method.

For example, if we take the two figures representing the state of affairs at 47° C. and 46° C. respectively (Fig. 16), we see that if crystallization takes place at 46° C., langbeinite and astrakanite cannot occur together in the strata; while if the temperature sinks lower to 46° C., they may appear as a mixture. Again (Fig. 17), at 31·5° C. kieserite and leonite cannot crystallize from the solution simultaneously; if they occur together in a stratum, the deposition must have taken place at 32° C. or above it.

The objection might be made that the effect of pressure might vitiate these conclusions, but van't Hoff investigated this point, and showed that even the highest possible pressures would be practically without influence.

We need not go into the details of van't Hoff's further researches upon the calcium salts and the borates; the experimental methods employed were similar to those with which we have dealt. It will be clear that these investigations of

[1] Van't Hoff, *Oceanischen Salzablagerungen*, i. p. 88.

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TABLE OF PARAGENESES.

	Langbeinite.	Vanthoffite.	$MgSO_4.6H_2O$.	Carnallite.	Leonite.	Glaserite.	KCl.	Kainite.	Kieserite.	Astrakanite
Thenardite	–[1]	above 46°	–	–	–	+[2]	–	–	–	to 49°
$MgSO_4.7H_2O$	–	–	to 31°	–	to 28°	–	–	to 27°	–	to 31°
Schönite	–	–	–	–	to 26°	to 26°	to 26°	–	–	to 26°
Loewite	above 43°	above 60°	–	–	47°–62°	above 57°	–	–	above 43°	43°–60°
Astrakanite	38°–47°	46°–60°	28°–36°	–	to 57°	to 60°	–	–	32°–49°	
Kieserite	above 37°	–	to 36°	+	32°–38°	–	above 72°	to 83°		
Kainite	37°–83°	–	to 32°	to 72°	to 55°	–	to 83°			
KCl	above 55°	–	–	+	to 61°	+				
Glaserite	above 61°	above 46°	–	–	26°–62°					
Leonite	37°–62°	–	27°–32°	–						

[1] The minus sign indicates that paragenesis is excluded between 25° C. and 83° C.
[2] The plus sign indicates that paragenesis is possible throughout the whole interval of temperature.

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van't Hoff and his collaborators have yielded us what we may

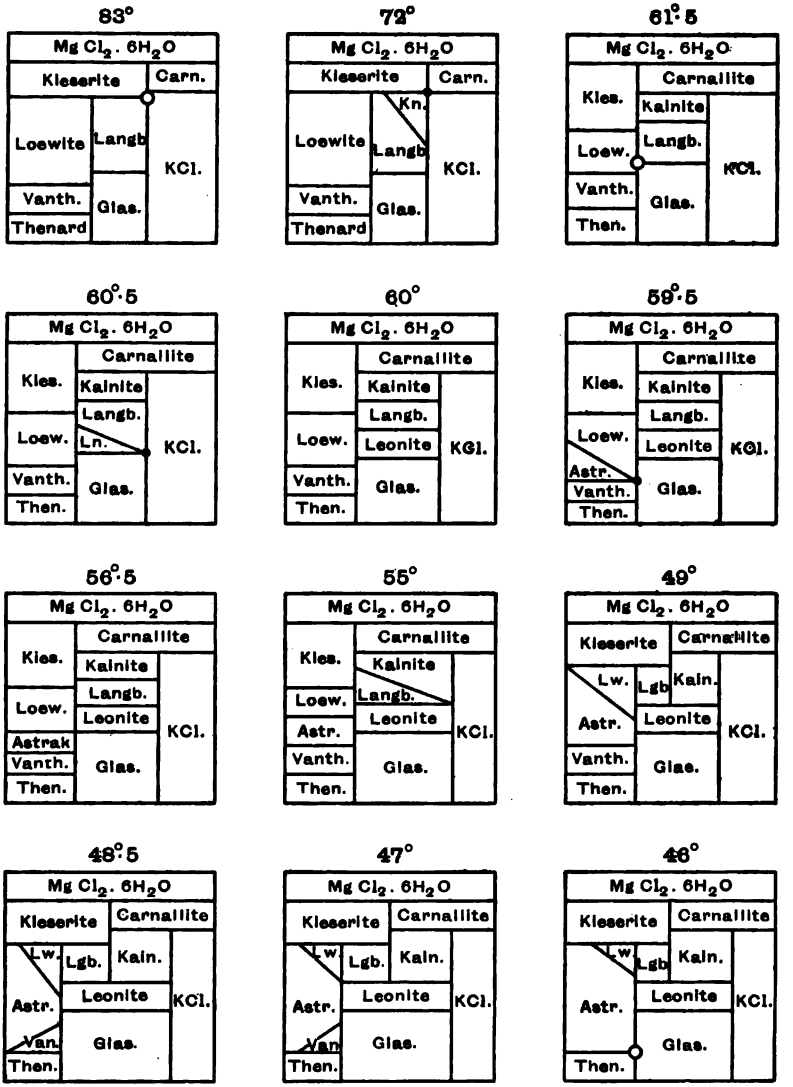

FIG. 16.

call a "geological thermometer," by whose aid we may determine the temperature which prevailed in the solution from

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which certain strata were deposited: and in certain cases this

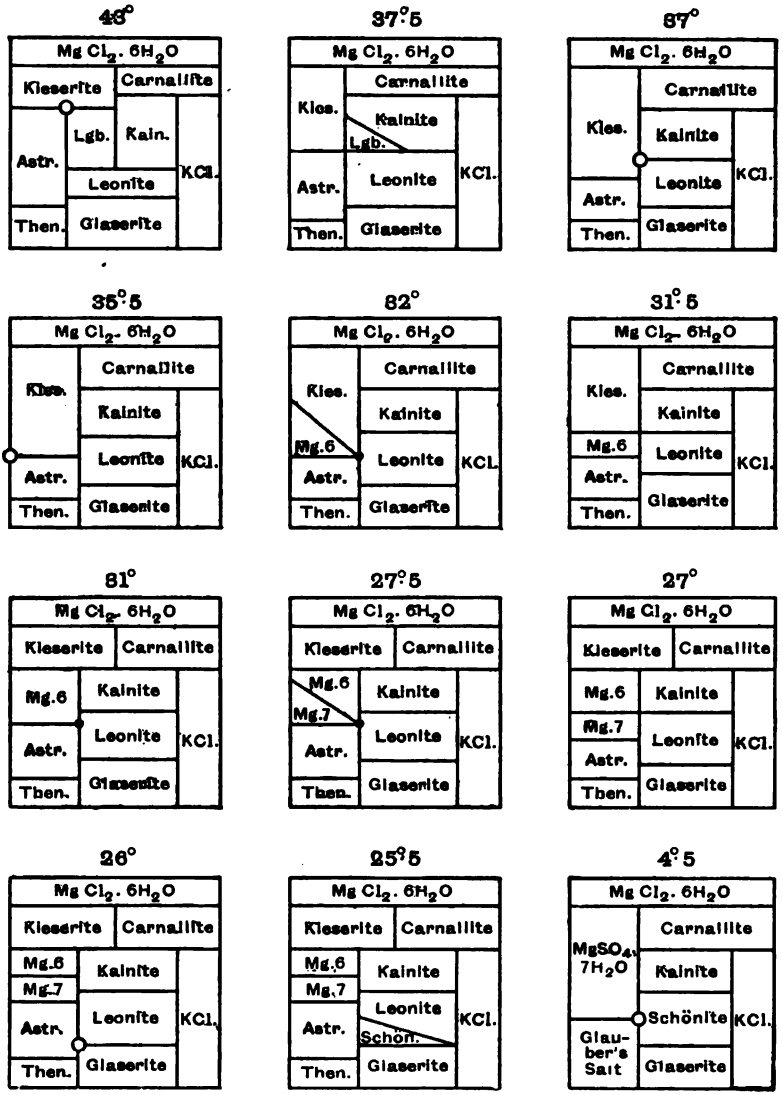

FIG. 17.

thermometer is so finely adjusted as to enable us to determine this temperature even to half a degree.

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CHAPTER III

ABSORPTION SPECTRA

1. General

When we endeavour to classify the physical properties of chemical compounds, we find that we can divide them roughly into two categories: colligative properties and non-colligative properties. The first of these groups comprises properties which are dependent purely upon the number of molecules present in the specimen we are examining; and of this type a good example is afforded by the pressure which a gas exerts at constant temperature. Non-colligative properties are in turn divisible into two sections: additive properties and constitutive properties. It is very difficult to draw a hard-and-fast line between these two sections, for most properties are partly additive and partly constitutive. When we speak of an additive property, we usually mean one in which the number of atoms of each element in the molecule is the preponderating factor; while we regard as constitutive properties those in which the additive properties are masked by the greater influence of the mode of linkage of atoms in the molecule.

It is self-evident that the study of additive properties is a much more simple line of research than the examination of constitutive properties. For instance, refractive index appears to be an additive relation, and its laws are already marked out in their main outlines; but when we take dielectric constant—which is simply the refractive index for waves of infinite length—the constitutive factor overwhelms the additive one, and up to the present time no definite relation has been traced between structure and dielectric constant.

Of all the constitutive properties of chemical compounds, the most complex appear to be absorption spectra. A few

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rough rules, some of which, like Armstrong's quinonoid hypothesis, are either mere words or obviously incorrect, are all that we have to guide us at the present time in tracing a connection between what is called "colour" and the chemical constitution of compounds. A considerable amount of time has been wasted in discussing the question of physiological colour, a phenomenon of very little scientific value, since it depends upon the crude perception of the human eye, which can be thrown out of gear by a dose of santonine, and which, at best, excludes more of the spectrum than it perceives. But even our finest instruments to-day probably include within their range only a very small portion of the complete electrical, thermal, and luminous spectrum of any substance.

When we look at the sun, we see what is called the visible solar spectrum, that is, white light. If we hold up between our eye and the sun a beaker containing ferric chloride solution, we shall see a yellow colour. Now, it is obvious that the ferric chloride solution has added nothing to the sun's light; so if it has produced a change in the light which reaches our eye, it is clear that the solution must have abstracted something from the solar spectrum. What actually happens is that some of the rays of the spectrum are absorbed in the solution, so that instead of the solar spectrum, we now see what is called the *absorption spectrum* of ferric chloride.

Suppose that instead of merely looking through the beaker, we place it in front of a spectroscope and pass the sun's light through the ferric chloride solution. By looking through the spectroscope we shall then find that, instead of the whole solar spectrum being transmitted, some of the lines are absent, having been absorbed by the ferric chloride. By comparison with the usual solar spectrum we could easily determine exactly which lines have been absorbed, and in this way we should have a more or less accurate idea of the absorption spectrum of ferric chloride. In practice, however, this method suffers from many drawbacks, and instead of it we use the following arrangement.

In Fig. 18 the apparatus is represented diagrammatically. E E are the electrodes of an arc light. C is a cell containing the solution whose absorption spectrum is to be measured. S is the slit of the spectroscope. P is the prism. O is a

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photographic camera, containing a plate, Q. The electrodes, E E, may be of any metal or alloy which gives a well distributed series of lines in its spectrum; an iron arc is sufficient for most purposes. The cell, C, must have quartz ends, through which the light of the arc may pass to the slit S. If glass ends were used, a very large proportion of the invisible ultra-violet part of the spectrum would be cut off; for though glass is transparent to the visible spectrum, it is almost opaque with respect to the ultra-violet region. The spectrum of the arc is thus thrown upon the plate Q, and by means of a diaphragm just in front of the plate it is reduced to a narrow band. With the usual form of photographic spectroscope, the band is about five inches long and a quarter of an inch wide.

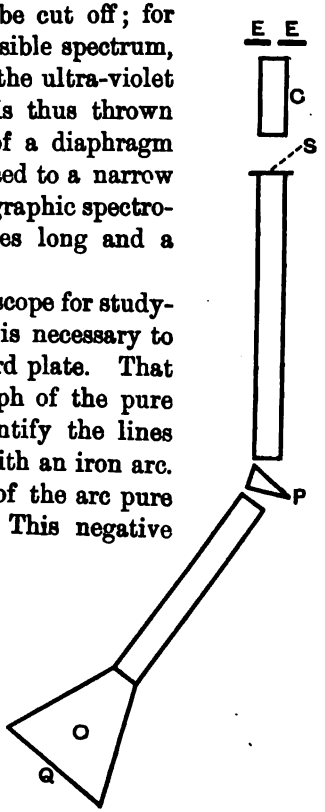

FIG. 18.

Before we can utilize the spectroscope for studying absorption spectra, however, it is necessary to prepare what we may call a standard plate. That is to say, we must have a photograph of the pure arc spectrum, and be able to identify the lines upon it. Suppose we are working with an iron arc. We first photograph the spectrum of the arc pure and simple, removing the cell C. This negative forms the basis of our standard plate. We then smear some salt, say lithium chloride, upon the arc, and take another photograph of the spectrum. In this new photograph we shall have not only the iron spectrum, but in addition to it the characteristic lines of the lithium spectrum. A comparison of the two negatives will enable us to detect the lithium lines. We now look up the tables of the lithium spectrum, and pick out one or two of the chief lines whose wave-lengths have been accurately determined. These lines we must next pick out on the lithium-iron plate. Having found them, it is clear that we shall be able to find some characteristic lines in the iron spectrum close to them. We look up the position of these iron lines in the table of the iron

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spectrum, and thus find the exact wave-length in that part of the spectrum. It is obvious that here we have a double control: the lithium spectrum and the iron spectrum. All that now remains to be done is to note with a mapping pen on the margin of the standard plate the exact wave-lengths of the lines in the iron spectrum whose position we have thus established. Other salts are smeared upon the arc, and a series of photographs containing iron spectra interspersed with characteristic lines of the spectra of other elements, is thus obtained. In this way we obtain the bearings, so to speak, of a series of points in the iron spectrum, and the intermediate points are filled in by interpolation.

Having now got our standard plate, we must proceed to apply it in mapping absorption spectra. We fill up the cell C, and adjust it so that the light of the iron arc passes through a tenth-normal solution of, say, quinone in alcohol of a certain thickness, *e.g.* 80 mm. We give an exposure of, say, fifteen seconds, and then develop the plate. On examination, the negative will be found to contain only part of the iron spectrum; for the quinone solution will have absorbed a portion of the rays. We lay the negative side by side with the standard plate, and are thus enabled to read off the wave-length at which the absorption begins.*

Instead of using wave-lengths, it is more usual to reckon in frequencies—that is, the reciprocals of the wave-lengths.

It is clear that the absorption spectrum which we obtain in this way is conditioned by three things: the length of the exposure; the strength of the solution; and the thickness of the layer through which we photograph. Taking the case of a tenth-normal solution of quinone as an example, we shall find the following. If we begin with a layer of solution 80 mm. in thickness, we find that all the spectrum beyond a frequency of about 2000 is absorbed (see Fig. 19, No. 1). When we reduce the thickness of the layer of solution in the cell to 70 mm., a somewhat peculiar phenomenon occurs. The

* The best modern spectrographs are provided with a scale of wave-lengths which can be photographed directly on the plate, side by side with the spectrum. In this way the frequent use of a standard plate is rendered unnecessary in actual practice; though the scale must be checked by means of a standard plate at intervals to make certain that it has not got out of adjustment.

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part of the spectrum to the left of 2000 comes through as before, but in addition to it a small portion of light is transmitted at a frequency of about 2800. This is shown in Fig. 19, No. 2. When we reduce the thickness of the layer in the cell

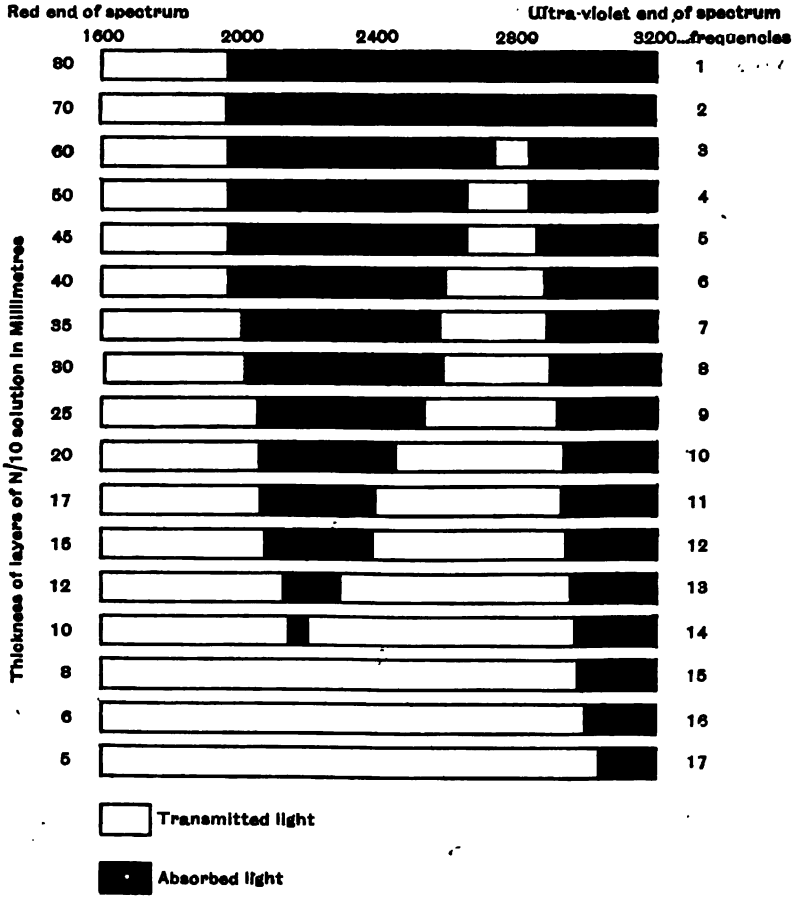

FIG. 19.

to 60 mm., we find that this band of light transmitted at 2800 is a little broader, and it continues to increase in breadth as we reduce the thickness of solution through which the light is passed. In the end (see Nos. 14 and 15) the light absorption between 2000 and 2800 becomes reduced to a minimum and

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finally disappears, so that we have complete transmission. The rough triangle of absorbed light extending from No. 2 to No. 14 in Fig. 19 is called an *absorption band*. It will be observed that this band has a portion of transmitted light on either side of it. When no second portion of the light is transmitted, as in No. 1, we have what is called *general absorption.** The extreme apex of the absorption band which is shown in No. 14 is called the *head* of the band. The raggedness of the line running down from the frequency 2000 is due to experimental error, and is brought about by the fact that the iron spectrum is not quite uniform.† Some of the lines are strong, and others are weak, so that the readings are influenced to some extent. A group of strong lines may be transmitted where the weaker ones would not appear, so that in some cases our readings are a little too high, in other cases a little too low.

Hartley was the first to see the value of results such as we have described. He pointed out that in this way we could obtain a map of the absorption spectrum of a compound which would serve to identify it completely, for each substance has its own particular type of absorption spectrum. Some give shallow bands, some deep, and some none at all, but only general absorption. Again, some substances have one band, some two, and others many.

It is clear that the diagram in Fig. 19 would be too clumsy a mode of reproducing the results obtained, and Hartley therefore devised what are called curves of molecular vibration. The ordinates in this system represent the thickness in millimetres of a given solution, say a tenth normal one, and the frequencies are plotted as the abscissæ. Baly and Desch[1] suggested that instead of the thickness being plotted on the ordinates, it would be more advantageous from some points of view to use the logarithms of the numbers representing the thicknesses, and this is the method now generally employed. Fig. 20 shows the molecular vibration curve of quinone in

* When an absorption band is present, we have what is called *selective absorption.*

† Hartley has employed electrodes composed of an alloy of lead, tin, and cadmium; the spark spectrum produced with this is practically continuous, and thus the disadvantages of the iron spectrum are avoided.

[1] Baly and Desch, *Trans.*, 1904, 85, 1029.

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alcoholic solution plotted in this manner. The data on which the curve is based are the same as those from which Fig. 19 was drawn. The head of the band lies near the intersection of the lines 40 and 2200. There is one other term which it may be advisable to make clear before proceeding further, viz. the *persistence* of the band. By this term we mean the change of dilution over which the band remains in existence. An examination of the figure will show that the band comes into existence just above the line 48 and disappears just below the line 40. It has therefore *persisted* over a change of dilution represented logarithmically by eight units.

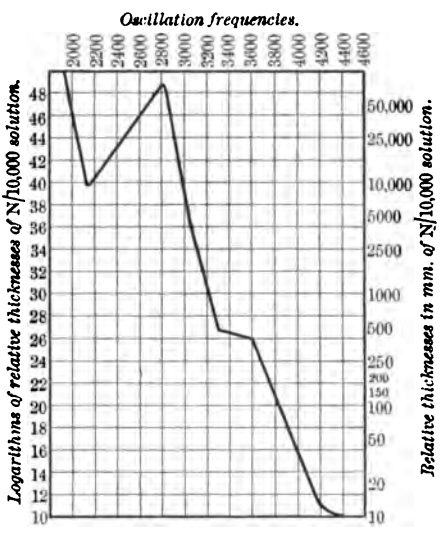

FIG. 20.

In the following section we shall discuss the application of this method of investigation to the determination of the constitution of substances which cannot successfully be dealt with by purely chemical means.

2. The Hartley Method

Among the most interesting compounds in organic chemistry are those which are termed tautomeric (or desmotropic, pseudomeric, phasotropic, merotropic, or isodynamically isomeric). Whatever name be applied to these substances, their chief characteristic is that an apparently homogeneous mother-substance can give rise to two isomeric derivatives according to the conditions under which the substitution reaction is carried out. The best known example of this class is the substance aceto-acetic ester, which is usually supposed to have the constitution—

$$CH_3—CO—CH_2—COOEt$$

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When this body is treated with sodium and then with methyl iodide, it produces a methyl derivative to which the following formula is ascribed :—

$$CH_3—CO—\underset{\displaystyle CH_3}{\underset{|}{CH}}—COOEt$$

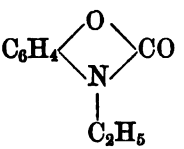
Here the methyl group is attached to one of the carbon atoms. If, on the other hand, we treat aceto-acetic ester in ethereal solution with diazomethane, we obtain an isomeric methyl derivative in which the methyl group is attached, not to carbon, but to oxygen—

$$CH_3—\underset{\displaystyle O.CH_3}{\underset{|}{C}}:CH—COOEt$$

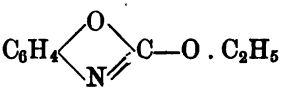
It appears, therefore, that aceto-acetic ester may react as if it had either of the two formulæ shown below—

$$CH_3—CO—CH_2—COOEt \qquad CH_3—\underset{\displaystyle OH}{\underset{|}{C}}:CH—COOEt$$

Now Hartley found that the replacement of hydrogen by a methyl or ethyl radicle produced very little change in the selective absorption of substances, except in some special cases. In general, the members of a homologous series show a slight increase in general absorption as we go up the series, but in other respects there is very little change in the spectra. But if we take the spectra of two such substances as the alkyl derivatives of ortho-hydroxy-carbanil, whose constitutions are represented below, we shall find that we have hit upon a case in which the replacement of a hydrogen atom by an alkyl radicle has made a considerable difference in the absorption spectrum—



Lactam form.



Lactim form.

The absorption spectra of hydroxy-carbanil and of the two

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ethyl derivatives (lactam and lactim forms) are shown in Fig. 20,* and it is evident on inspection that we have here two different types of absorption spectra. The spectrum of the lactam-compound differs completely from that of the lactim-ether. Now, when we compare the spectrum of the mother-sub-

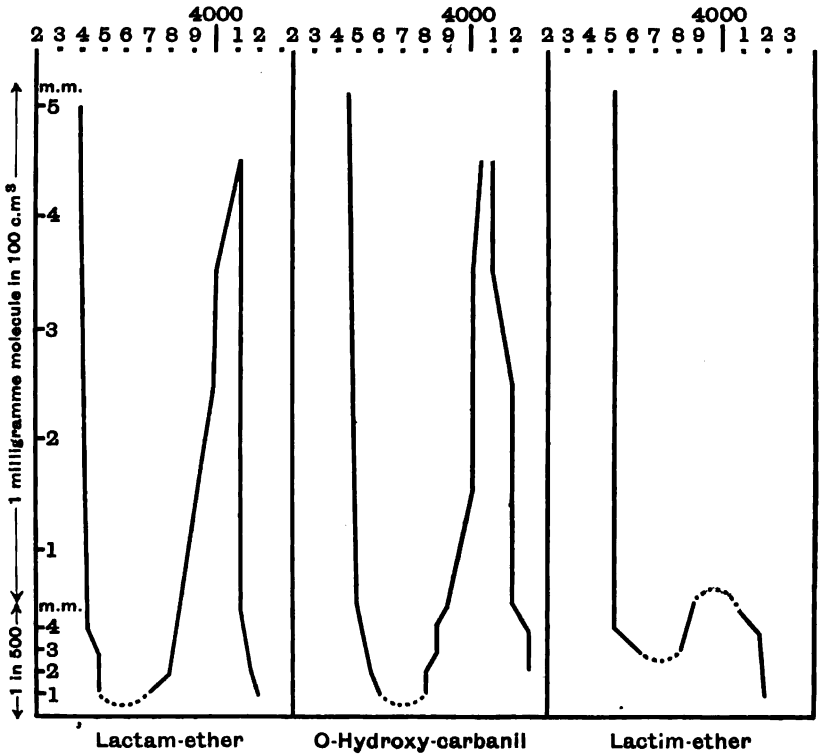

FIG. 21.

stance with those of the derivatives, it is obvious that it resembles the spectrum of the lactam-body rather than that of the lactim-ether. From this, Hartley deduces that the mother-substance must have a constitution resembling the lactam-form rather than one akin to the lactim-type. We should, therefore,

* The curves are reproduced from Hartley's work, and it should be noted that the ordinates represent thicknesses of solution, and not logarithms of thicknesses.

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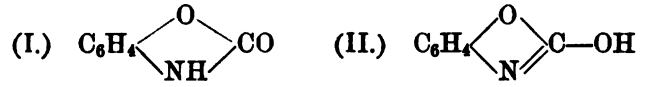
ascribe to hydroxy-carbanil the constitution (I.) rather than (II.)—



This gives some idea of what is known as the Hartley method of determining the constitution of organic compounds. It has proved itself of great importance in many cases, and is certainly one of the most accurate in the solution of these problems.

3. The Benzene Spectrum

It will be remembered that during the last generation, organic chemistry has entered upon a new stage in its career. Half a century ago, the arrangement of atoms within a molecule was supposed to be more or less rigid, and even Kekulé was unable to shake this fixity in the minds of his generation. Since his day, however, things have progressed a little; we no longer regard atoms as fixed points, but rather as bodies vibrating about mean positions; and the benzene formula, which Kekulé described as a system in vibration, has once more become dynamic, after a considerable static existence. Even after Kekulé had shown the way, various authors put forward suggestions for rigid benzene formulæ. Amongst these we need mention only Claus, Dewar, Armstrong, Thomsen, Ladenburg, and Sachse.

In 1897, Collie[1] described a benzene space formula based upon the idea that benzene was a system of twelve atoms, all of which were free to vibrate either about their own axes or about mean positions in space; and he showed that by means of this model the older rigid formulæ could be represented merely as phases in the vibrations of the benzene molecule. Several years later, Collie,[2] in conjunction with Baly, examined the absorption spectrum of benzene, with which we must now deal.

Hartley and Huntington[3] photographed the absorption

[1] Collie, *Trans.*, 1897, 71, 1013.
[2] Baly and Collie, *Trans.*, 1905, 87, 1332.
[3] Hartley and Huntington, *Phil. Trans.*, 1879, 170, i. 257.

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spectrum of benzene, and described it as containing seven bands in the ultra-violet region. Later, Hartley and Dobbie found only six bands. A re-examination of a considerable number of photographs of the spectrum [1] led to the conclusion that Hartley and Huntington were correct, and that the spectrum of benzene contains seven bands and not six. The difficulty of detecting and identifying the seven bands was considerable, for, as can be seen from Fig. 21, they are situated very close to one another, and are very narrow.

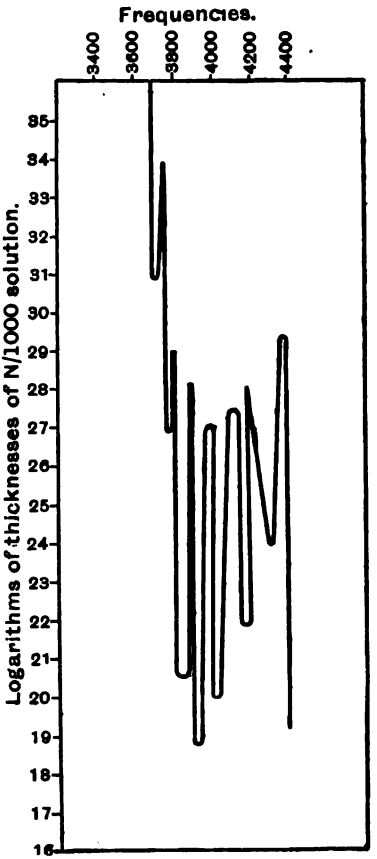

FIG. 22.

We must now turn to the theoretical views put forward to explain this series of phenomena. Baly and Collie started from the assumption that the bands in the absorption spectrum of benzene were due to a making and breaking of linkage between the carbon atoms of the benzene ring. When we speak of a change of linkage, however, we perhaps run the risk of being misunderstood. What is really meant is that a variation in the amount of affinity exerted between two atoms takes place. From this it is clear that we must ascertain the number of the different possibilities of attraction between any two atoms in the benzene ring; for it is evident that all the atoms of a closed system must exert some effect—even though it be only a small one—upon each other. We have thus to find out how many pairs of atoms, each different in character from the others, we can find in the benzene system. In point of fact,

[1] Baly and Collie, *Trans.*, 1905, **87**, 1332.

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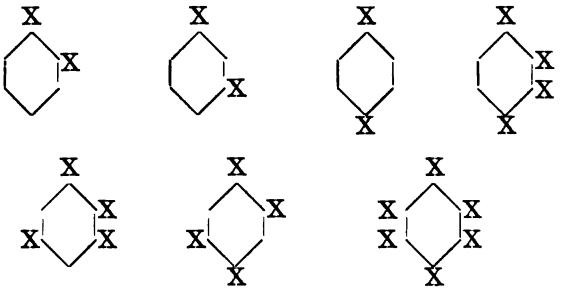
there are three such pairs: for the carbon atoms may be in the ortho-, meta- or para- positions to each other; there is no fourth arrangement possible. We must then take into account the fact that two of these exchanges may synchronize, which would give rise to a new type of vibration whose period would probably differ from any of the original three. Examination will show that there are three such possibilities, viz. when the atoms 1, 2, 3, 4 or 1, 2, 3, 5 or 1, 2, 4, 5 are simultaneously undergoing change of linkage. Finally, we have a seventh case, in which all six atoms of the benzene nucleus are exchanging affinity at the same time. These seven phases of linkage change are represented below, the atoms which are supposed to be changing their linkage being marked X—



Each of these possible phases of linkage-change differs from the others to such an extent as to make it not unreasonable to suppose that the vibration set up by each will differ from the others sufficiently to produce a different band in the absorption spectrum.

The vibrations of Collie's space formula for benzene make it clear how the required alteration in affinity could occur in each of the seven cases, but of course there is no possibility at present of our being able to refer each of the seven bands to its proper source. Such a task would require very many more experimental data than we have yet at our disposal.

It seemed of some interest to examine the absorption spectra of hexasubstituted derivatives of benzene in which all the hydrogen atoms are replaced by six similar atoms or groups. In this way we obtain a new substance which is as symmetrical as benzene, and it was thought that new light might be thrown upon the vibrations of the benzene system. Crymble, Stewart

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and Wright[1] examined the spectra of several derivatives of this type, and found that the result of the substitution was to blurr the seven bands, a broad absorption band taking their place. From this it appears that even groups with so little residual affinity as the ethyl radicle are capable of interfering very markedly with the exchange of affinity which may be supposed to take place between the atoms of the benzene system.

4. The Problem of General Absorption

In recent years the study of absorption spectra has been for the most part confined to those questions which centre round the selective absorption of organic compounds, and it is not difficult to trace the causes which have led to this concentration of attention upon a particular section of the subject. The problem of the origin of colour in organic bodies attracted the attention of chemists both from the theoretical and, in the case of dye-stuffs, from the technical standpoint. Now, visible colour depends to a very considerable extent upon the presence in the visible region of absorption bands; and when the work of Hartley had brought the investigation of the ultra-violet region into prominence, it was natural that the idea of colour should be enlarged to include bands in the invisible ultra-violet as well as the corresponding phenomenon in the visible region. And since in the visible region the hardest-fought controversy from the chemical point of view had centred round the presence or absence of absorption bands, it was only to be expected that similar discussions would arise as to the meaning of the numerous bands which were soon found to exist in the ultra-violet section of the spectrum. A second cause of the preference shown for the investigation of selective absorption is easy to detect. When we are dealing with substances which show absorption bands, a very slight alteration in their chemical structure is sufficient to produce a marked alteration in the character of the banded spectrum; and it is this delicacy which makes selective absorption so fascinating to those who delight in theory-making. General absorption, on the other hand, is by no means so readily affected by minute constitutional changes. An examination of the curves on p. 49 will show

[1] Crymble, Stewart and Wright, Unpublished observation.

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that while the bands in the spectra of the lactam and lactim ethers of hydroxy-carbanil are totally different in character, the general absorptions of the two substances differ but little from each other. Thus in the case of selective absorption we are dealing with a property which is susceptible to extremely minute influences; while in general absorption we have to do with forces which must differ markedly from each other before we can detect their effects.

When a compound is studied by the organic chemist there are seven chief questions which demand an answer:

1. What elements does the molecule contain?
2. In what proportion are the various elements present?
3. What is the number of the atoms in the molecule?
4. In what order are the atoms linked together?
5. Is the substance saturated or unsaturated?
6. How are the unsaturated centres of the molecule related to each other?
7. What is the arrangement in space of the atoms within the molecule?

Each of the factors indicated in the above questions enters into the problem of general absorptive power; and for the sake of convenience we may take them up in turn.

With regard to the influence of the various elements upon general absorption, it is impossible to lay down any hard-and-fast rules. Saturated open-chain hydrocarbons are usually distinguished by being extremely diactinic; and the introduction of halogen atoms into the molecule generally tends to increase the power of absorbing light. When we turn to other elements such as nitrogen, sulphur, or phosphorus, we complicate the problem by the introduction of unsaturation; so that it is hard to estimate the exact part played by the new element. The question is of considerable importance, however, and it is to be hoped that some investigator may find time to throw some light on the point.

From the point of view of spectroscopy, the second question is so closely connected with the first that no progress can be made in this direction until the first problem is in a much more advanced stage.

Turning now to the influence of the number of atoms in a molecule, we come to the question of homologous series. It

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has been found that if we examine the spectra of the methyl, ethyl, propyl and butyl derivatives of a given substance, the power of general absorption increases as we go up the series. This was established in 1879 by Soret and Rillet[1] in the case of the alkyl nitrates; and it appears to be a general property of homologous series. Each atom in a compound seems to exert a small amount of absorptive power, and by adding atom to atom we eventually obtain quite a marked effect on the spectrum.

We next come to the fourth point, the manner in which the atoms are linked together within the molecule; and here, again, if we confine our attention to saturated substances the data are very sparse. Crymble, Stewart and Wright[2] have found that in the case of the alkyl bromides the normal substance has a much weaker power of absorption than the isomeric iso-form. For example, normal propyl bromide (I.) is much less absorptive than iso-propyl bromide (II.):

$$CH_3 . CH_2 . CH_2 . Br \qquad (I.)$$

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad CH . Br \\ \diagup \\ CH_3 \end{matrix} \qquad (II.)$$

Results of this type might indicate that a symmetrically built molecule has more absorptive power than an isomeric molecule in which the groups are unsymmetrically distributed.

When we take up the question of the influence of unsaturation upon the general absorptive power of molecules, the data are very full.[3] It has been established, largely by the monumental researches of Hartley, that if we compare the spectra of a saturated and an unsaturated hydrocarbon, the unsaturated substance will greatly surpass the saturated one in its power of absorbing light. Since cyclic carbon chains are really unsaturated bodies, it might be expected that this class would show a higher absorptive power than open-chain bodies, and this has been found to hold good. With regard to the influence of the triple bond upon absorption there are very few data available; but it appears[4] that its effect is not so strong as that of the ethylenic linkage.

[1] Soret and Rillet, *C.r.*, 1879, **89**, 747.

[2] Crymble, Stewart and Wright, Unpublished observation.

[3] Hartley, *Brit. Assoc. Report*, 1908.

[4] Stewart, *Trans.*, 1907, **91**, 199; Ley and Engelhardt, *Zeit. physikal. Chem.*, 1911, **74**, 311.

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We must now pass to the question of the effect produced by the introduction into the molecule of more than one unsaturated group; and at this point we reach a branch of the subject in which chemical constitution plays a very important part.

One of the best known characteristics of ethylenic bonds is their faculty of uniting with one molecule of bromine to form a dibromo-derivative, thus—

$$\begin{array}{l} CH_3—CH=CH—CH_3 \\ \qquad\quad Br—Br \end{array} = \begin{array}{l} CH_3—CH—CH—CH_3 \\ \qquad\quad\ \ Br\quad Br \end{array}$$

Let us now take the case of a substance containing two double bonds which are separated from one another by the interposition of one or more methylene groups. If to a gramme molecule of such a compound we add one gramme molecule of bromine, we shall find that the halogen is absorbed by one of the double bonds, while the second double bond remains intact, thus—

$$\begin{array}{l} CH_3—CH : CH—CH_2—CH : CH—CH_3 \\ \qquad\quad Br—Br \end{array} = \begin{array}{l} CH_3—CH—CH—CH_2—CH : CH—CH_3 \\ \qquad\qquad\quad\ \ Br\quad Br \end{array}$$

This is a perfectly normal behaviour; but if no methylene group be interposed between the two double bonds we obtain quite a different result, for instead of the halogen atoms attacking *one* of the double bonds they attack both simultaneously, and a new double bond is formed as shown below—

$$\begin{array}{l} \overset{1}{CH_3}—\overset{2}{CH} : \overset{3}{CH}—\overset{4}{CH} : \overset{5}{CH}—\overset{6}{CH_3} \\ \qquad\quad Br——————Br \end{array} = \begin{array}{l} \overset{1}{CH_3}—\overset{2}{CH}—\overset{3}{CH} : \overset{4}{CH}—\overset{5}{CH}—\overset{6}{CH_3} \\ \qquad\qquad\quad\ \ Br\qquad\qquad\ \ Br \end{array}$$

It will be seen from the formulæ that the original double bonds lay between the atoms 2, 3 and 4, 5; while in the final substance there is a new double bond in the 3, 4-position.

Thiele,[1] from a study of many systems of this type, put forward his theory of "partial valencies." He assumes that in a double bond between two carbon atoms the whole of the

[1] Thiele, *Annalen*, 1899, **306**, 87.

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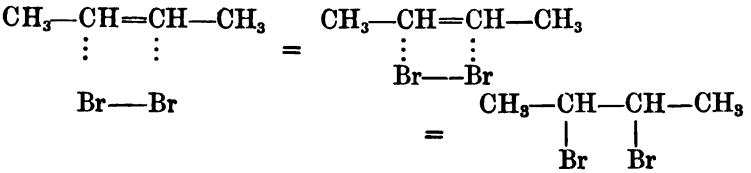
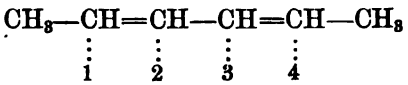
available affinity of the atoms on each side of the double bond is not completely neutralized in the union, but that a certain amount remains free. This free affinity he terms a "partial valency," and he assumes that this partial valency serves to anchor any fresh atoms which come within range of the system. Once anchored, the presence of the new atoms causes a re-arrangement of affinity within the two molecules, with the result that the new atoms enter the system and reduce the double bond. If we represent the partial valencies by dotted lines, the steps in the process could be expressed by the formulæ below—



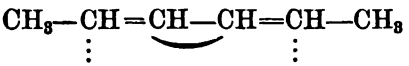
When we come to a system of the type—

$$R—CH : CH—CH : CH—R$$

we have what Thiele terms a system of "conjugated double bonds," and he explains the abnormal behaviour of this system in the following way. Since, under his postulates, the addition of new atoms to a system can take place only after they have been anchored by the partial valencies of the system, it is clear from experimental results that in a compound of the following type—



only the partial valencies 1 and 4 are active. We are therefore driven to assume that the valencies 2 and 3, acting across the single bond, neutralize each other in some way, and are thus thrown out of action.* This state of affairs Thiele represents by the following scheme—



* The close agreement between this theory and actual experience is found in the case of benzene, where all the double bonds are conjugated in a single system with no free partial valencies. Hence, theoretically, benzene is not a true unsaturated body, and it is well known that experiment bears this out.

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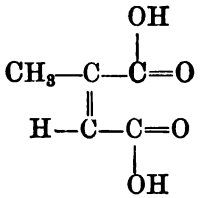
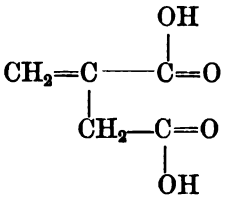
Such a grouping as this is anomalous not only from the chemical point of view but also in its influence upon the physical properties of compounds in which it occurs.[1] Brühl.[2] found that it had a marked effect upon refractive power, producing higher values than the calculated refractivities; Hilditch[3] traced the same influence in the case of optical rotatory power; analogous results were observed by Pascal[4] in diamagnetism; and Sir W. H. Perkin[5] proved that similar effects could be detected in magnetic rotation.

Crymble, Stewart, Wright, and others[6] have examined the spectra of numerous pairs of isomeric substances, one set containing isolated double bonds, while the isomeric bodies contained a conjugated grouping; and they find that in every case the substance which contains the conjugated system is much more absorptive than the isomeric body in which the double bonds are not so completely joined together in a single system. For example, citraconic acid contains three double bonds joined together in a single conjugated system; whereas in the isomeric itaconic acid one of the double bonds is separated from the rest by the interposition of the methylene group—



Citraconic Acid.



Itaconic Acid.

Citraconic acid has a greater power of absorbing light than is shown by itaconic acid.

From this it is clear that when two unsaturated groups occur in a molecule in such positions that they are able to

[1] For a full discussion of this question see Smiles' "Relations between Physical Properties and Chemical Constitution," 1910.

[2] Brühl., *Ber.*, 1907, **40**, 878.

[3] Hilditch, *Trans.*, 1909, **95**, 831, 1570, 1578; 1910, **97**, 1091; Edminson and Hilditch, *ibid.*, 1910, **97**, 223.

[4] Pascal, *C.r.*, 1909, **149**, 342.

[5] Sir W. H. Perkin, *Trans.*, 1896, **69**, 1141.

[6] Crymble, Stewart, Wright, and Glendinning, *Trans.*, 1911, **99**, 451; Crymble, Stewart, Wright, and Miss Rea, *ibid.*, 1911, **99**, 1262.

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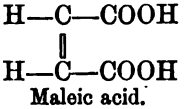
exercise a reciprocal influence upon each other, their joint effect upon the absorptive power of the substance is very much greater than when they are separated from each other by neutral atoms. One centre of residual affinity increases the absorptive power to a considerable extent as compared with a saturated compound; two isolated centres in turn augment the compound's general absorption; while a still greater power is produced by the co-ordination of the two centres into one system.

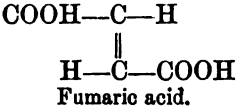
We must now pass to a consideration of the effect of stereo-isomerism upon general absorption. The spectra of compounds containing asymmetric carbon atoms have been examined by Magini[1] and by Stewart[2] with the following results. Two optical antipodes have exactly similar absorption spectra; meso-tartaric acid has a greater power of general absorption than either active tartaric; while the spectrum of racemic acid shows a power of absorption greater than that of dextro-tartaric and less than that of meso-tartaric acid. Turning to the question of geometrically isomeric carbon compounds, the same authors have shown that maleic and citraconic acids possess a much less light-absorbing power than the isomeric bodies fumaric and mesaconic acid—

Least absorbent.

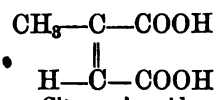


Maleic acid.

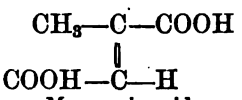
Most absorbent.



Fumaric acid.

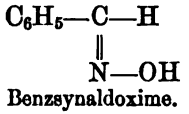


Citraconic acid.

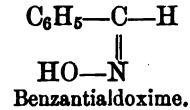


Mesaconic acid.

Hartley and Dobbie[3] found that the spectra of the two stereo-isomeric oximes of benzaldehyde were identical.



Benzsynaldoxime.



Benzantialdoxime.

At first sight it appears strange to find this difference in

[1] Magini, *J. chim. phys.*, 1904, **2**, 408.
[2] Stewart, *Trans.*, 1907, **91**, 1537.
[3] Hartley and Dobbie, *Trans.*, 1900, **77**, 509.

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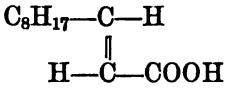
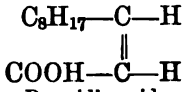
behaviour between the isomers containing an ethylenic bond and those which contain the linkage —N : C :, but a consideration of the formulæ of the various substances in the light of what has already been described in the preceding paragraphs will throw some light upon the point. We have already learned that general absorption is greatly influenced by the presence in the molecule of some unsaturated centre; and that when we have two unsaturated centres in a substance the absorptive power depends to a great extent upon their mutual interaction. Now the change from maleic to fumaric acid entails the shifting of one unsaturated carboxyl group with respect to the other; and the same is true of the change of citraconic into mesaconic acid: so that in both these cases we are to a great extent altering the interplay of forces in the molecule. Similar arguments hold good in the case of the change of active tartaric acid into the meso-form, for here also the relative positions of the carboxyl groups are altered. When we come to the two oximes, however, the case is different, for there the two groups which change their relative positions in space are the phenyl and hydroxyl radicles. The phenyl group certainly possesses a marked degree of residual affinity; but the influence of the hydroxyl radicle on general absorption is very feeble, as is proved by the very low absorptive power of the aliphatic alcohols. Hence we might expect that these two groups would influence one another but slightly, and that a change in their relative positions would produce no marked difference in the absorptive power of the molecule. Support has been lent to this view by an examination of the absorption spectra of brassidic and erucic acids[1] which were found to have almost identical powers of absorption.



Erucic acid.



Brassidic acid.

It will be seen that in this case we have altered the relative positions of the groups —COOH and —C_8H_{17}; the first of these is an unsaturated centre, but the second is a saturated group,

[1] Crymble, Stewart, Wright and Arbuthnot, Unpublished observation.

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so that no great change in the absorptive power is to be expected on the above hypothesis.[1]

5. Valency and Absorptive Power

In the course of his study of the relations between the physical properties of elements and their places in the periodic system, Carnelley noted that under certain limitations the colour of a compound depends to some extent upon the atomic weights of the constituent elements. For instance, if we take compounds AX, BX, CX, etc., where A, B, C, etc. represent successive elements belonging to the same sub-group in the periodic table, and X is any other element, then we shall find that, as we pass from the light element A through the heavier element B to the still heavier element C, the colours of the compounds deepen in tint. For example, let us take the case of the halogen compounds of cobalt and nickel.

$CoCl_2$	Blue	$NiCl_2$	Yellow
$CoBr_2$	Green	$NiBr_2$	Golden yellow
CoI_2	Black	NiI_2	Black

Here, as we pass from the chlorine atom, with an atomic weight of 35·5 to the iodine atom with an atomic weight of 127, we find that the colour deepens from blue to black in the case of cobalt salts, and from yellow to black in the case of the corresponding nickel derivatives. Again, if we take the case of salts in which the acidic part remains constant throughout the series while the metal is replaced in rotation by the next higher member of the same sub-group, we get similar results.

NaI	White	AgI	Light yellow
CuI	Cream-coloured	AuI	Golden yellow

This rule seems to be of fairly general application, but as it refers to substances in the solid condition, it is possible that the state of aggregation exercises a considerable influence. This might account for several of the exceptions to the rule which have been observed.

Crymble[2] has approached the subject from a stand-point

[1] Ley, *Beziehungen zwischen Farbe und Konstitution*, 1911, has made a similar suggestion with regard to selective absorption.

[2] Crymble, *Proc.*, 1911, **27**, 68.

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which evades this difficulty. On photographing the absorption spectra of potassium chloride and potassium sulphate, he found that ten millimetres of a normal solution of either salt was diactinic. This proves, of course, that all the ions present in the solution under such conditions are diactinic. Hence it is clear that the colour of solutions of copper chloride or copper sulphate must be due to the copper ion. Taking as a standard a ten-millimetre thickness of a normal solution of a salt or a length of solution containing an equivalent amount of the metal, Crymble regards a compound as "diactinic" when under these conditions light is transmitted up to a wave-length 2300.

He finds that under this definition metallic ions may be grouped into three classes :—

A. Non-absorptive ions. This class includes the following metals :—

Li, Na, K, Be, Mg, Zn, Cd, Ba, Al, and Th.

B. Ions showing general absorption only. In this class are :— .

Hg, Tl, Sn, Pb, Sb, and Bi.

C. Ions showing selective absorption. In this class may be placed :— .

Cu, Ce, Mn, Fe, Au, Cr, U, Co, Pt, Ti, and V.

Now, if we examine the metals placed in Class A, it is obvious that all of them possess a fixed valency : lithium, for example, forms only one chloride. The metals which show absorption (Class B and Class C), are all capable of exhibiting a change in valency : tin forms stannous and stannic chlorides, while copper forms cuprous and cupric salts. Thus it is established that metallic elements which are capable of exerting two degrees of valency have a much greater power of absorption than those metals which do not yield more than one chlorine compound.

A comparison of the majority of the elements in Class B and Class C will show that here also we can trace a general rule ; for the elements in Class C, whose ions show selective absorption, yield two series of salts in which the valency of the metal changes its valency by a single unit :—

$FeCl_2$ and $FeCl_3$ $CrCl_2$ and $CrCl_3$ $MnSO_4$ and $Mn_2(SO_4)_3$

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whereas in the case of the metals in Class B, which show general absorption only, the change of the "ous" form to the "ic" form entails a change of *two* units in the valency :—

$TlCl$ and $TlCl_3$ $SnCl_2$ and $SnCl_4$ $SbCl_3$ and $SbCl_5$

It is not yet certain whether this second generalization will hold good in every case; but the first rule put forward by Crymble marks a great advance in our knowledge of the subject.

If we apply to this problem of the metallic ions the results which we arrived at from our examination of the effect of unsaturation upon absorptive power in organic substances, we might be led to assume that the metallic atoms contain certain centres of residual affinity which are called into play by the combination of one atom with another. In the case of atoms such as sodium and potassium, which are capable of exhibiting one valency only, we might imagine that they contained only one such centre. In the case of atoms showing more than one valency, however, it seems possible that the atom may include two centres of residual affinity, which may act like two conjugated double bonds in an organic compound, and by their interplay may increase the absorptive power of the substance just as we found in the case of organic bodies.

6. The Spectroscopic Determination of Chemical Change

Dobbie, Lauder, and Tinkler[1] have shown how spectroscopic measurements may be used to throw light upon the extent to which chemical change takes place in a solution, and also upon the relative strengths of two reagents which have the same chemical effect. The substance used by them in this research was cotarnine, which is capable of existing in two forms. What the structures of these two forms are is of no importance to us at the present time; considerable controversy has centred round the point. All that we need remember for our present purpose is that the change of one form into the other takes place under the influence of alkalis, while the reverse change is produced by acids.

In aqueous solution, cotarnine is yellow; that is to say, it

[1] Dobbie, Lauder, and Tinkler, *Trans.*, 1904, **85**, 121.

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has an absorption band in the visible region. Now, when the aqueous solution is treated with alkali, the yellow colour disappears, the amount of colour change being proportional to the quantity of alkali present. To compare the strengths of various alkalis, therefore, it is only necessary to add fixed quantities of them to a given solution of cotarnine, and estimate spectroscopically the change which they bring about in the substance.

In this way, Dobbie, Lauder, and Tinkler arrived at the results shown in the table below. The figures represent the percentages of the ammonium form of cotarnine which is converted into the carbinol form in presence of the corresponding amount of alkali.

Strength of base.	KOH.	LiOH.	NaOH.	$Ba(OH)_2$.	$Ca(OH_2)$.	NH_4OH.
N/1	98·5	98·5	98·5	—	—	45
N/2	97·5	97·5	97	—	—	40
N/3	96·5	96·5	95·5	—	—	30
N/4	95	94	94	—	—	—
N/6	93	93	93	—	—	25
N/7	92·5	—	92·5	—	—	—
N/8	91	92·5	91	90	—	—
N/10	89	90	89	—	—	20
N/20	83	82·5	82·5	—	—	—
N/50	67·5	70	70	67·5	67·5	10
N/100	52·5	57·5	52·5	52·5	50	—
N/200	42·5	42·5	40	40	40	—
N/400	25	20	20	20	20	—
N/600	20	20	20	20	20	—

The possible applications of this method are, of course, almost inexhaustible; and it would be quite feasible to enlarge its scope and make it a means of measuring reaction velocities.

7. Conclusion

In the foregoing sections we have described one or two of the more interesting researches which have been carried out recently in this field. It will be seen that in some cases the experimental basis upon which the theoretical views have been raised is apparently not of sufficient breadth to allow us to accept the theories themselves with perfect confidence; but this is, of course, the case with all branches of science in their earlier period. At the present time, spectroscopic research may

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be divided into several categories. In the first place, we have a series of investigators who photograph spectra apparently with no idea beyond finding out what the absorption curve looks like. This work is pretty much on a par with that of the organic chemists who apply somebody else's reaction to the iso-propyl derivative when the lower members of the series have already been made; it may eventually be of use to some one, but that will not be the fault of the man who carries it out. Then there is a second class of spectroscopists who apply the Hartley method without seeming to recognize the fact. These, at least, may do work of some practical value, even though it be not very original. Finally, there are two classes of workers whose researches are tending to bring spectroscopy into touch with chemical problems. The first of these concern themselves with the relation between spectroscopic measurements and other physical properties of organic substances, such as refractive index, optical rotatory power, magnetic rotation, and so forth. The second class of investigators endeavour to link their spectroscopic results with their chemical reactions, in order to find out whether there be any connection traceable between the two phenomena. In either of these directions there appears to be a fruitful field awaiting research.

At the same time, it must be remembered that great care must be taken in the building up of hypotheses. In all the chemical field there is no subject which lends itself more to this than does spectroscopy; but it cannot be too often stated that hypotheses which are not backed by chemical evidence of their correctness are worse than useless. Further, the substitution of vague generalities for definite statements may do considerable harm. It is true that in some cases we know so little of the processes which go on within the molecule, that we are forced to express ourselves in general terms; but it should be our aim to come as soon as possible to some definite conclusion in the matter, and put forward something which can be tested —something which is not mere verbiage and an excuse for dodging round a dialectic corner as soon as people begin to look into the subject.

One of the most promising fields at the present moment appears to be the study of the influence of solvents upon absorption spectra. If it were possible to carry out a long series of

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experiments in which attention was paid to the physical properties (such as dielectric constant) of inert solvents, one can hardly doubt that some important results would follow. Another branch of the same subject is the influence of the solvent upon reaction-velocities, and here it might be possible to detect a parallelism between the action of the solvent upon the reacting bodies and its action upon their spectra.

Again, spectroscopy furnishes us with a means of watching the changes which take place while a reaction is going on in a solution; and it seems probable that interesting results might be acquired by a study of reactions which may or may not involve the formation of an unstable intermediate product, or of those which result in intramolecular change.

A field which appears to have been barely touched is the examination of analogous compounds of similar elements. For example, it might be of interest to discover whether there was any relation between the absorption spectra of an alkyl ether, a sulphide and a selenide and the chemical properties of the three substances. Parallel results might be found in the examination of derivatives of tri- and penta-valent nitrogen, phosphorus and arsenic. In the "onium" salts, also, the spectra might throw some light upon the cause of the ionization of the negative radicle.

At the present time we are ignorant of the cause of colour in many of the simplest substances. For example, if nitrogen and hydrogen, both colourless gases, be combined, we get a colourless gas, ammonia, formed. But if for hydrogen we substitute oxygen, we get a brown gas, NO_2, which on polymerization gives us a much more weakly coloured body, N_2O_4. It is clear that in cases such as these one atom has the effect of stimulating another into a state of vibration, while other atoms have not this power. One nitrogen atom cannot stimulate a second, nor can a hydrogen atom stimulate a nitrogen one; an oxygen atom cannot produce marked colour by combining with a hydrogen atom. But a nitrogen atom can apparently produce colour when united with an oxygen atom in certain ways. Analogous results are to be found among organic substances. For example, the grouping (I.) does not appear to produce visible colour, while compounds containing the grouping (II.) are usually strongly coloured.

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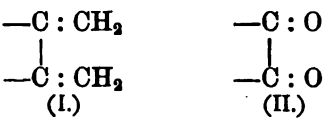

(I.) (II.)

Both of these groupings contain residual affinity which is capable of attracting four hydrogen atoms, so that it is not merely a question of the amount of unsaturation, but rather one of kind, with which we have to do. A study of this problem would certainly yield useful results.

We need not describe any further subjects for research; many others will suggest themselves to the reader. In the last year or two, a considerable increase of interest in this branch has manifested itself among chemists, but it is to be hoped that other workers may be tempted into this field of research.

At the present day, the problem of what is termed residual affinity is rapidly being forced to the front in many widely different lines of investigation, and it is becoming more and more evident that our ordinary graphic formulæ are reaching the end of their usefulness. As an expression of the purely chemical behaviour of compounds they have played a wonderful part on the chemical stage, and in the future they will no doubt aid us in this as well as any substitute which can at present be imagined. But when we come to the relation between chemical constitution and physical properties the ordinary graphic formula, devised as it was to suit a totally different set of circumstances, cannot be blamed if it fails to throw much light on the question. What will be required in future is a standardization of what we describe as residual affinity, and it appears possible that spectroscopy may aid us in this line. Assuming the electronic basis of matter, we are driven to regard the chemical, electrical and physical properties of a compound as different facets of a whole, or as interpretations of the electrons' motions in terms of various crude measurements with different units. At the present time our measurements of residual affinity are in the atomic stage, that is to say, we ascribe to both an ethylenic bond and a carbonyl group the same amount of residual affinity since they are both capable of combining with two hydrogen atoms. If it were possible to apply some spectroscopic measure of residual affinity, we should be in possession of a much finer measuring instrument,

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and it is not improbable that the differentiation between one compound and another in this way would lead to valuable results. Ordinary chemical means can carry us only to the confines of the atomic world, but for a true understanding of the whole field we must be able to penetrate into the sub-atomic, or electronic universe, for it is in this region that the real changes occur which we measure in the ordinary chemical reaction.

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CHAPTER IV

THE PSEUDO-ACIDS

1. Introductory

If we attempt to draw up a rough classification of electrolytes, the first three categories which suggest themselves are—

1. Acids, which give rise to hydrogen ions.
2. Bases, which yield hydroxyl ions.
3. Salts, which dissociate into acidic and basic ions.

To these three classes we must add a fourth, amphoteric electrolytes, a series of substances which are capable of producing either hydrogen or hydroxyl ions according to the experimental conditions. Amphoteric electrolytes might be sub-divided into two sections: for in one set of these bodies it is found that the same group of atoms gives rise to both hydrogen and hydroxyl ions owing to ionization taking place in two different ways; while in the second set the hydrogen ions are liberated from one part of the molecule, and the hydroxyl ions from another. Examples of the first class are found among the hydroxides of metals such as lead, aluminium, chromium, beryllium and tin, which are soluble in both acids and alkalis; while the second class is represented by bodies like amido-acetic acid—

$$NH_2.CH_2.COOH$$

whose carboxyl group furnishes hydrogen ions, while the basic radicle $—NH_2$ forms the origin of the hydroxyl ions.

In recent years an additional class of electrolytes has been studied, which have been named pseudo-acids and pseudo-bases; and the present chapter will be devoted to a description of the acids and their properties. Before entering into details, however, some account must be given of the history of the subject.

When an alkyl iodide is treated with silver nitrite it usually

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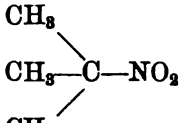
gives rise to two isomeric substances, a nitro-paraffin and an alkyl nitrite. For example, if we use ethyl iodide, we obtain nitro-ethane and ethyl nitrite—

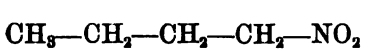
$C_2H_5.NO_2$	$C_2H_5.O.N:O$
Nitro-ethane.	Ethyl nitrite.

With the latter substance we are not concerned here.

The nitro-paraffins were discovered in 1872 by Victor Meyer,[1] and in the course of his investigations he observed that they dissolved readily in alkaline solutions. This pointed to the possibility of their containing a hydrogen atom which was capable of being replaced by a sodium atom; and in accordance with the views current at that time, Victor Meyer inclined to the explanation that the "negative" nitro-group influenced the neighbouring hydrogen atoms so strongly as to make them acidic to some extent. This idea was tested by preparing a tertiary nitro-paraffin, and that substance was found to yield no sodium salt.



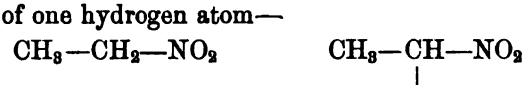
Tertiary.



Normal.

An examination of the two formulæ above will show that in the normal substance the carbon atom next the nitro-group has two hydrogen atoms attached to it, whereas in the tertiary body the nearest hydrogen atom is separated from the nitro-group by two carbon atoms. It was therefore assumed that the nitro-group only influenced a hydrogen atom in its immediate vicinity.

In those days, it was taken for granted that the structures of an acid and its salt were analogous, and thus the first formulæ for the alkali derivatives of the nitro-paraffins were written simply by substituting the symbol for the alkali atom in place of one hydrogen atom—



Nitro-ethane. Sodium derivative.

[1] V. Meyer, *Annalen*, 1874, 171, 1.

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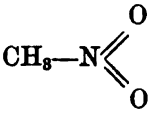
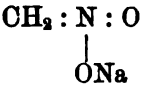
This view held the field for a considerable period, but in 1888, Michael,[1] in the course of his work on the constitution of acetoacetic ester, was led to challenge the validity of this assumption. According to him, when a metallic atom replaces a hydrogen atom in an organic compound, it will attach itself to an oxygen atom in preference to a carbon atom, owing to the greater "negativity" of the former. We cannot enter here into his arguments; a full account of the controversy will be found in Lachman's *Spirit of Organic Chemistry*. Applying Michael's ideas to the case of nitro-methane, we should obtain the following formulæ for the parent substance and the sodium derivative:—



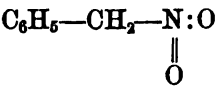
Nitro-methane.



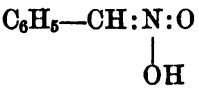
Sodium derivative.

On this assumption, the constitution of the acid cannot be deduced from that of the salt merely by replacing the sodium symbol by the hydrogen symbol; but we must assume that the two bodies differ very considerably in constitution from each other.

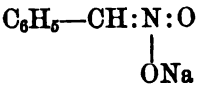
In 1895, the problem became still more complicated from the experimental standpoint, for in that year Holleman,[2] Hantzsch and Schultze,[3] and Konowalow[4] independently discovered that nitro-paraffins could be obtained in two isomeric forms, the normal form and the *aci*-form, the latter of which had the same structure as the sodium salts. Thus in the case of phenyl-nitro-methane, the following substances were discovered:—



Normal nitro-paraffin.



Aci-form.



Salt.

This discovery vindicated Michael's views, and the further investigations of Hantzsch carried the subject into a new field.

[1] Michael, *J. pr. Chem.*, 1888 [2], **37**, 507.
[2] Holleman, *Rec. trav. chim.*, 1895, **14**, 129.
[3] Hantzsch and Schultze, *Ber.*, 1896, **29**, 2193.
[4] Konowalow, *Ber.*, 1896, **29**, 699.

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The substance which Hantzsch and Schultze first examined was the phenyl derivative of nitro-methane, which has the structure shown below—

$$C_6H_5—CH_2—NO_2$$

This body is formed by the action of silver nitrite upon benzyl iodide; and in its purification the sodium salt is prepared, and then decomposed by dilute acetic acid or carbonic acid. The substance obtained by this method is a liquid boiling at 225°–227° C.

If, instead of weak acids, we use fairly strong mineral acids to decompose the sodium salt, and take care that the temperature of the solution does not rise during the operation, we obtain, instead of the oil, a crystalline body of M.P. 84° C. This substance is the *aci*-form of phenyl-nitro-methane, and has the structure—

$$C_6H_5—CH : N : O$$
$$\quad\quad\quad

indifferent, non-conducting normal form. If no secondary reaction took place, it is clear that in the end the conductivity should reach that of a solution of sodium chloride containing the same amount of sodium as the original sodium salt, as this is decomposed by the hydrochloric acid to produce sodium chloride. In practice, however, it is found that the isomeric change of *aci*-form into the normal form is accompanied by a slight decomposition of the nitro-body, which produces traces of benzoic acid and nitrous acid; so that the end-conductivity of the solution is influenced by the presence of these electrolytes in addition to the sodium chloride formed in the main reaction. The following figures[1] will give some idea of the velocity of the reaction.

Equimolecular solutions of hydrochloric acid and the phenyl-nitro-methane sodium salt, each at a dilution $v = 32$, were mixed together, producing a dilution $v = 64$. The temperature of the mixture rose from 0° C. to about 2° C., but in the following figures a correction for this has been made:—

After	3 minutes	μ	= 69·6
,,	5 ,,	μ	= 68·1
,,	20 ,,	μ	= 67·0
,,	60 ,,	μ	= 63·7
,,	95 ,,	μ	= 62·7
,,	145 ,,	μ	= 62·1
,,	180 ,,	μ	= 62·0 (constant)

For NaCl under same conditions $\mu = 60$

An examination of the conductivities of solutions of other nitro-methane derivatives showed that the normal nitro-compound in aqueous solution had practically the same conductivity as pure water, whereas the *aci*-derivatives were acids probably stronger than acetic acid.

Let us now summarize what we have dealt with in the foregoing paragraphs. In the first place, it has been shown that derivatives of nitro-methane exist in two isomeric forms, one of which shows neutral properties, while the other isomer is markedly acidic in character. Secondly, the conversion of the neutral body into the salt (which is a derivative of the acidic form) requires a certain time; this is shown by the different rates at which the two substances dissolve in alkalis: the

[1] Hantzsch and Davidson, *Ber.*, 1896, **29**, 2259.

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converse change of salt into the neutral form of the nitro-compound is also a comparatively slow reaction; this is proved by the conductivity measurements which were given above. Thus in the nitro-paraffin series we have an example of substances which can, by intramolecular rearrangement, become acidic. Such substances Hantzsch defines as *pseudo-acids*. There is another class of compounds which can, by intramolecular change, give rise to basic substances. These Hantzsch terms *pseudo-bases*. It should be noted that Hantzsch lays especial stress upon the point of intramolecular change and not upon the neutral character of one of the isomers. For example, he would include quinone monoxime in the class of pseudo-acids on the ground that intramolecular change takes place in the course of salt-formation, the form (I.) being converted into the salt (II.), instead of the salt (III.) being formed as one might expect from the acidic character of the —N . OH group.

$$\underset{\text{(I.)}}{O:C_6H_4:N.OH} \qquad \underset{\text{(II.)}}{NaO.C_6H_4.N:O} \qquad \underset{\text{(III.)}}{O:C_6H_4:N.ONa}$$

When we mix a solution of an ordinary acid with that of a base, the velocity of neutralization is immeasurably rapid; but in the case of a pseudo-acid, since intramolecular change must occur and convert the pseudo-acid into the *aci*-form before neutralization can begin, it is evident that the neutralization will not be an "instantaneous" reaction, but will be governed by the velocity of the intramolecular change. This Hantzsch defines as *slow neutralization*.

2. Hantzsch's Criteria

In one of his earlier papers on the subject of pseudo-acids, Hantzsch[1] put forward a series of criteria by means of which he suggested that it was possible to establish whether or not a substance was a pseudo-acid. Some of these criteria have since been abandoned as inapplicable; but we may give the original list here, reserving a discussion of each for the later sections of this chapter.

I. When a hydrogen compound shows slow neutralization phenomena it is a pseudo-acid.

[1] Hantzsch, *Ber.*, 1899, **32**, 575; 1906, **39**, 2109.

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* II. When a hydrogen compound which itself shows little or no conductivity, produces a neutral alkali salt which is either not hydrolyzed or only exhibits slight hydrolysis, then this salt has a constitution different from that of the original hydrogen compound—*i.e.* the latter is a pseudo-acid.

III. When a colourless hydrogen compound (which when dissolved in water gives a colourless solution) yields coloured ions and alkali salts which retain their colour in the solid form, it is a pseudo-acid.

† IV. If in conductivity measurements of a tautomeric substance it is found that the temperature-coefficient is abnormally large and increases with a rise in temperature; or if the dissociation constant varies to an abnormal extent with change in temperature, it indicates that the substance in question is a pseudo-acid.

V. (*a*) If a substance which in its normal form contains no hydroxyl group can be induced to react with acetyl chloride or phosphorus penta-chloride with the liberation of hydrochloric acid, it is a pseudo-acid.

* (*b*) If a hydrogen compound does not form a salt by direct addition of ammonia but only does so indirectly—*i.e.* in conjunction with water—then the hydrogen compound is a pseudo-acid.

VI. The existence of abnormal hydrates ‡ in the case of tautomeric bodies is a chemical indication that the corresponding water-free substances are pseudo-acids which only produce salts indirectly by the previous formation of an addition-compound of the hydrate type.

† VII. The molecular conductivity of all electrolytes in aqueous-alcoholic solution is reduced if the alcohol content of the solution be increased while the degree

* These criteria have since then been proved to be invalid.

† These criteria are of very limited application.

‡ Abnormal hydrates are defined by Hantzsch as those which are not formed by direct addition of water to the non-hydrated substance, but are produced only after the original substance has undergone chemical change, *e.g.* when it is precipitated from salts, etc.

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of dilution is kept constant; but the diminution of the conductivity of true acids is greater under the same conditions than is the case with pseudo-acids.

It should be expressly stated that Hantzsch admits that no one of these criteria in itself is a conclusive proof of the presence of a pseudo-acid. All that can be said for them is that if a compound agrees with several criteria, then the probability is that it is a pseudo-acid. Further, the various criteria vary in decisiveness. Hantzsch in one of his papers[1] laid especial stress upon the neutralization phenomena, the ammonia reaction, and the formation of coloured ions by colourless parent substances; while he attached much less importance to the other criteria.

In the succeeding sections we shall take up in turn the various criteria, and give some account of the criticisms which they have evoked.

3. The Phenomena of Slow Neutralization

Some description of the slow neutralization phenomena has already been given in the first section of this chapter. Experimentally, the question may be approached from either of two points. In the first place, we may prepare a solution of the sodium salt of a nitro-paraffin, say nitro-ethane, and add to it the molecular equivalent of hydrochloric acid. If the dilution be considerable and the temperature be kept in the neighbourhood of zero, it is found that at the moment of the addition the conductivity is considerably higher than that of a solution of sodium chloride under the same conditions. This increase in conductivity above that of a common salt solution is to be attributed to the presence of the *aci*-form of nitro-ethane, which results from the double decomposition—

$$CH_3.CH{:}NO.ONa + HCl = NaCl + CH_3.CH{:}NO.OH$$

The presence of the *aci*-form is also shown by the fact that at the moment of mixing the two solutions, the mixture is acid and gives a coloration with ferric chloride. After a few hours, however, the conductivity sinks to that of an equivalent solution of pure sodium chloride; while simultaneously the solution loses its acid properties and ceases to give any ferric chloride

[1] Hantzsch, *Ber.*, 1906, **39**, 2109.

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coloration. This is to be attributed to the conversion of the *aci*-form into the neutral nitro-compound—

$$CH_3.CH{:}NO.OH \rightarrow CH_3.CH_2.NO_2$$

The second method depends upon the slow formation of the nitro-paraffin salt. Equimolecular aqueous solutions of nitro-ethane and sodium hydrate are mixed together; and it is found that the conductivity does not immediately attain that of the sodium salt of nitro-ethane. Whence we may deduce that salt-formation is not instantaneous, but requires a measurable time to complete.

Now, though the slow neutralization phenomena give us a clue to the presence of a pseudo-acid, it must not be assumed that the converse proposition also is true. Because a body does not show slow neutralization we are not entitled to take for granted that it is not a pseudo-acid. It is clear that what we actually measure in the case of slow neutralization is the rate of change of the normal form into the *aci*-form, or *vice versâ*. But if this change took place with very high velocity, it is quite possible that it might be complete before we could measure the conductivity. In this case, we might actually be dealing with a pseudo-acid, but conductivity measurements might lead us to suppose that we had a true acid instead. Thus this criterion of Hantzsch holds good only if we obtain positive results. If the conductivity measurements do not demonstrate the presence of a pseudo-acid we are not entitled to assume that the substance is not pseudo-acidic.

4. Abnormal Hydrolysis

The evidence upon which Hantzsch[1] was induced to put forward this criterion for pseudo-acids may best be given in his own words. "The potassium salt of dinitro-ethane reacts completely neutral and is no more hydrolytically dissociated than, *e.g.*, potassium chloride. Such salts, however, as I will show by numerous examples, are derived from strong or at least moderately strong acids (of the same strength as the acetic acid group) which have a clearly marked acidity; for very weak acids produce hydrolytically dissociated salts with an

[1] Hantzsch, *Ber.*, 1899, **32**, 579.

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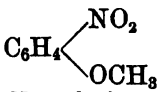
alkaline reaction. Now free dinitro-ethane has not a medium, or even a very small, dissociation constant; it has absolutely no measurable dissociation constant at all. Thus it is not merely an acid weaker than very weak acids like hydrocyanic acid or phenol; it is not an acid at all. Now if it, acting as an acid, could produce a salt $CH_3.CK.(NO_2)_2$ then this salt would be hydrolysed to a greater degree than even potassium cyanide or sodium phenolate. Since, however, the actual so-called salts of dinitro-ethane show absolutely no hydrolysis, they cannot be derived from unaltered dinitro-ethane, but must be produced from an isomeric acid form, iso-dinitro-ethane."

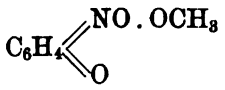
Unfortunately for this reasoning, it was shown by Kauffmann[1] that it is in contradiction with the Law of Mass Action. Assuming this law, it can be proved that in spite of salt formation being accompanied by intramolecular change the hydrolysis of the salt will be normal. Thus this criterion falls to the ground.

5. Colour Change in Passing from Pseudo-Acid to Salt

It will be recalled that Hantzsch laid down as one of his criteria, that if a colourless hydrogen compound gives rise to coloured ions and coloured solid alkali salts, then it is a pseudo-acid. At the time this was first put forward, the only evidence in favour of it was physico-chemical, and no purely chemical data were forthcoming for a considerable period. In order to prove chemically that a compound is capable of existing in two isomeric forms it is essential to isolate two isomeric derivatives from the parent substance, and it was not until 1906 that Hantzsch and Gorke[2] were enabled to announce that this criterion had been put upon a purely chemical basis by the isolation of two methyl ethers of *o*-nitrophenol. These two bodies resembled in character the isomeric ethers of phenyl-nitro-methane, and to them the following formulæ were ascribed:—



Normal ether.



Ether of *aci*-form.

[1] Kauffmann, *Zeit. physikal. Chem.*, 1904, **47**, 618; cf. Euler, *Ber.*, 1906, **39**, 1607.

[2] Hantzsch and Gorke, *Ber.*, 1906, **39**, 1073.

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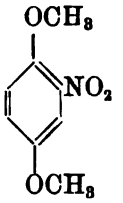
The first substance is a colourless compound, while the *aci*-ether is of an intense red tint. Thus the intramolecular change which produces the *aci*-form from the normal nitro-phenol is accompanied by a change in colour.

Some remarks of Hantzsch [1] in reference to the auxochrome view of colour in this connection led to a somewhat prolonged controversy with Kauffmann [2] into the details of which we need not enter here. Kauffmann adduced the case of the dimethyl ether of nitro-hydroquinone, which, according to him,[3] is capable of giving both coloured and colourless solutions, though, as can be seen from its formula, no isomeric change is probable in the molecule.



Kauffmann stated that in ligroin solution the substance is colourless; but that on allowing it to crystallize, intensely yellow needles are obtained. Other solvents, especially associating solvents, gave pale yellow solutions, while dissociating solvents, such as glacial acetic acid, water or alcohol, gave more deeply coloured solutions. Thus, according to Kauffmann, "in dissociating solvents, the solute shows its natural properties most clearly, in associating solvents, on the contrary, it is in a state of strain." This last phrase will, of course, appear to furnish a complete explanation or to be mere words, according to the reader's prejudices.[4] Hantzsch in his reply pointed out that Kauffmann's assumption was not in accordance with our experience. In dissociating solvents we do not find a substance showing its "normal" behaviour, for in such solutions we get dissociation or addition compound formation. Hantzsch then proceeded to examine the molecular weight, colorimetric value and molecular refraction of

[1] Hantzsch, *Ber.*, 1906, **39**, 1084.

[2] Kauffmann, *Ber.*, 1906, **39**, 1959, 4237; 1907, **40**, 481, 4547; *see also* Hantzsch, *Ber.*, 1906, **39**, 3072; 1907, **40**, 1556, 1572; 1908, **41**, 1214.

[3] Kauffmann, *Ber.*, 1906, **39**, 4240.

[4] Hantzsch, *Ber.*, 1907, **40**, 1556.

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nitro-hydroquinone dimethyl ether in various solvents, and found that it was probable that the yellow solutions of the body contained molecular complexes. If this be the case, and since the solid substance is also yellow, it seems fair to assume that the yellow colour sometimes shown by the substance is due to the formation of complexes and is not inherent in the molecule; and hence Kauffmann's case falls to the ground.

Further evidence in this direction is furnished by some work of Blaise [1] who showed that when glutaconic ester—

$$COOEt—CH_2—CH:CH—COOEt$$

is treated with sodium ethylate, it gives a yellow colour, whereas if a homologue which contains no free hydrogen atom is treated with sodium ethylate no colour is developed. This points to the wandering of a hydrogen atom during the addition of the ethylate, the addition compound being supposed to have the following structure :—

$$COOEt—CH:CH—CH:C\begin{matrix}ONa\\OEt\end{matrix}$$

It seems probable, on the evidence before us, that this criterion of a pseudo-acid is valid.

6. Abnormal Temperature Coefficients

In his original paper on the pseudo-acids, Hantzsch [2] expressed this criterion in the following words: "Temperature coefficients of conductivity which are abnormally large and which increase with rise in temperature, as well as degrees of dissociation and dissociation constants which vary to an abnormal extent with temperature-change, indicate in the case of tautomeric bodies the presence of ionization-isomerism."

It will be seen that the kernel of the question lies in the word abnormal; and from the polemics of Hantzsch and Euler, it appears that this expression is capable of rather wide interpretations.

Hantzsch [3] based his views upon the assumption that true

[1] Blaise, *Bull. soc. chim.*, 1908, **29**, 1028.
[2] Hantzsch, *Ber.*, 1899, **32**, 579.
[3] *Ibid.*

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acids, which do not alter their constitution, show an increase of conductivity with rise in temperature; but that this increase is small and is to be considered as due to an increase in ionic mobility rather than to an increase in the degree of ionization. Further, according to him, in the case of true acids, the conductivity temperature coefficients diminish with rise in temperature. Finally, the dissociation constants of acids of unchangeable constitution are not dependent to any great extent upon temperature, since in the aromatic acids between 0° C. and 25° C. it does not usually exceed about ten per cent., sometimes positive and sometimes negative. In contrast to this behaviour, Hantzsch places that of the pseudo-acids, which, according to him, between 0° C. and 25° C. show an increase of a hundred per cent. or more in the constant.

In his criticism of Hantzsch's views, Euler[1] pointed out that a comparison of the temperature coefficient of a pseudo-acid like phenyl-nitramine with those of true electrolytes such as aniline or phenol shows that the latter bodies have a much higher coefficient.

Hantzsch in his reply[2] objects to the comparison of a weak electrolyte with such a substance as dinitro-methane, which is ten times as strong as acetic acid. He admits, however, that nitro-form, which is undoubtedly a pseudo-acid, has almost the same low coefficient of temperature as hydrochloric acid.

Without going further into the question, it is evident that this criterion cannot stand by itself, but can be used only in support of other evidence. It should be noted, however, that Hantzsch has expressly stated this in his earlier papers: none of his criteria in itself is sufficient to *prove* the presence of a pseudo-acid; all that can be done is to show the probability that a substance belongs to this class.

7. The Ammonia Reaction

This criterion depended upon the rate of precipitation of an ammonium salt from a solution in absolute benzene. Solutions of the pseudo-acid and of ammonia in benzene were mixed together under certain conditions and it was found that a slow

[1] Euler, *Ber.*, 1906, **39**, 1607.
[2] Hantzsch, *Ber.*, 1906, **39**, 2098.

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precipitation of ammonium salt took place, which was in sharp contrast to the immediate precipitation produced when benzoic acid was substituted for the pseudo-acid. Further investigations, however, convinced Hantzsch[1] that the factor of supersaturation entered so powerfully into the question as to make the criterion of little value.

8. Abnormal Hydrates

When a substance forms a hydrate it is usually assumed that direct addition of water to the molecule occurs; but in certain cases it is possible that before water can attach itself to the substance, the latter body must undergo intramolecular change. Such hydrates are defined by Hantzsch[2] as "abnormal," and their presence can be taken as a proof that the compounds which yield them are capable of tautomeric change. Let us suppose that a substance is capable of tautomeric change and gives rise to a hydrate. By substitution we can alter the structure of the molecule so as to prevent this tautomerism, while still retaining the general character of the substance. If this derivative gives no hydrate, then we should be justified in assuming that the hydrate formation was in some way bound up with the possibility of tautomerism; and we might suppose that tautomeric change must occur before the hydrate could be formed. In this case, of course, the parent substance would be a pseudo-acid. Instead of the addition of water, we might utilize the addition of alcohol as a test; the reasoning in the case of alcoholates is the same as that used for hydrates. It will be seen that the possibility of applying this criterion is very limited.

9. Conductivity in Aqueous-alcoholic Solutions

Hantzsch and Voegelen[3] observed that if a pseudo-acid and a real acid be dissolved in mixtures of alcohol and water, the dilution of the solution being kept constant while greater percentages of alcohol are added, then the diminution of the

[1] Hantzsch, *Ber.*, 1907, **40**, 3084.
[2] Hantzsch, *Ber.*, 1899, **32**, 579.
[3] Hantzsch and Voegelen, *Ber.*, 1902, **35**, 1001.

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conductivity of the true acid with increase of alcohol is less than the falling off in the dissociation of the pseudo-acid. A concrete example will make the point clear. Suppose we compare the conductivities of violuric acid and lævulinic acid at v_{64}. The two acids are approximately of the same strength, for with violuric acid K = 0·0027, while lævulinic acid has K = 0·0024.

Percentage of alcohol in solution	0%	25%	40%	50%	75%	100%
Violuric acid μ_{64}	14·50	6·53	4·13	2·91	0·90	0·23
Lævulinic acid μ_{64} . . .	13·85	4·65	2·35	1·49	0·32	——

An examination of the figures will show that when the solution contains say forty per cent. of alcohol, in the case of violuric acid the original figure 14·50 has fallen to 4·13, whereas in the case of lævulinic acid the fall has been greater, from 13·85 to 2·36. Thus through the same change of character of the solutions we have produced a drop of 10·37 units in the case of violuric acid and 11·49 units in the case of lævulinic acid. In other words, the pseudo-acid has shown less decrease in conductivity than the true acid.

This criterion is not applicable in every case, for Euler[1] has shown that phenyl-nitramine and acetic acid give practically the same results, as the following figures for K. 10^6 prove:—

	Water	40% Alcohol
Phenyl-nitramine	17·5	1·26
Acetic acid	17·8	1·86

To this, Hantzsch[2] retorts that the criterion does not necessarily hold in the case of every pseudo-acid; all that we need say is that if a substance agrees with it, then that substance is a pseudo-acid. If the substance does not show the phenomena it may or may not be a pseudo-acid; and further tests must be applied if we are to determine its nature.

10. The Refractometric Method

In the foregoing sections we have dealt with the criteria laid down by Hantzsch in the course of his researches on the pseudo-acids. There remains one other method, devised by

[1] Euler, *Ber.*, 1906, **39**, 1607.
[2] Hantzsch, *Ber.*, 1906, **39**, 2098.

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Muller,[1] which enables us to determine whether a pseudo-acid is present. It is well known that in many cases it is possible to calculate the refractive index of a given substance by simply adding together a series of known factors which correspond to the atoms and linkages of the substance's molecule. This method breaks down when tautomeric change is possible within the molecule, as then we might get an observed value corresponding to either form of the compound's structure or to a mixture of the two forms. In such cases it is often possible to determine the exact constitution of the substance observed, even when it consists of a mixture of two isomerides.

Now suppose that we have an acid RH yielding a sodium salt RNa which is formed without intramolecular transposition, it is clear that if we take the difference of the refractivities of RH and RNa under identical conditions this difference will depend entirely upon the H and Na, that is, the difference will be a constant for all normal acids. This constant difference has been found to be approximately 1·6. Let us now consider the case of a pseudo-acid. Here, not only have we the replacement of hydrogen by sodium, but in addition we have an alteration of the compound's structure due to the change of the pseudo-acid into the true acid previous to salt formation. This change in structure is accompanied by a considerable alteration in refractivity, so that in the case of the pseudo-acid we should expect to find that the difference between the refractivity of the parent substance and that of the salt would diverge considerably from the normal difference of 1·6 units. This has actually been found to be the case by Muller. Taking into account the accuracy with which refractivity measurements can be made, this method of proving the presence of a pseudo-acid appears to possess considerable advantages over most of the others.

11. Conclusion

We have now discussed the various criteria which may be applied to determine whether or not a given substance should

[1] Muller, *C.r.*, 1902, **134**, 664; *see also* his article in *Récents progrès de la chimie* (2nd Series), 1906, p. 40.

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be ranked as a pseudo-acid or as a normal acid. Some of Hantzsch's original suggestions have proved of no value, and it is clear that others are either of little use or of very limited application. The most valuable ones seem to be the phenomena of slow neutralization, the change of colour in passing from a pseudo-acid to its alkali salts, and the refractometric method. Of less importance are the temperature coefficients, the formation of abnormal hydrates, and the conductivity decrease in aqueous-alcoholic solutions. The ammonia reaction and the supposed abnormal hydrolysis of pseudo-acids have been proved to be worthless.

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CHAPTER V

COLLOIDS

1. General

Graham,[1] in the course of his researches on diffusion, came to the conclusion that a substance in solution may belong to either of two classes. The first of these divisions contains those compounds which can easily be induced to crystallize, and which diffuse rapidly through animal membranes. The second class of substances does not form crystals, and their velocities of diffusion are very markedly less than those of the other (crystalline) bodies. To distinguish the one class from the other, we designate the former as *crystalloids* and the latter as *colloids.*[2] The name is derived from κόλλα, glue being a very good example of the colloidal type.

It will be remembered that if we add an acid to a solution of sodium silicate, a flocky gelatinous precipitate of silicic acid is thrown down from the solution; but that if, on the other hand, we pour a solution of silicate into concentrated hydrochloric acid, no such precipitate appears. Phenomena such as these led Graham to recognize two subdivisions of his colloid class. The first of these sections contained the colloid solutions, such as that of silicic acid in strong hydrochloric acid; to these he gave the name *sols.* In the second section he placed the actual colloid precipitates, which, from their gelatinous nature, he designated as *gels.*

Graham found that colloids could be formed in solutions other than aqueous, and this necessitated a slight addition to his nomenclature. Where the liquid medium was water, he termed the bodies *hydrosols* and *hydrogels;* when the liquid was alcohol, the substances were named *alcosols* and *alcogels;* other fluids were described in analogous ways.

[1] Graham, *Annalen*, 1862, **121**, 1; *Ann. chim. phys.*, (iv.) 1864, **3**, 121.

[2] For a full treatment of this subject, see Wo. Ostwald's *Grundriss der Kolloidchemie*, 1911.

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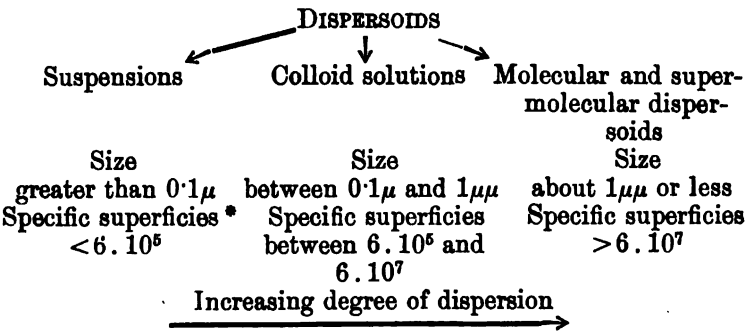
In recent years, considerable advances have been made in the study of colloidal solutions, and it is now known that they consist of two phases: a liquid and a series of liquid or solid particles which float in the liquid. This has given rise to a new nomenclature and classification of colloid systems. Using the ordinary phase rule nomenclature, we speak of the solution as a heterogeneous system; the liquid is termed the *dispersion medium;* and the suspended particles are called the *disperse phase.* Wo. Ostwald uses the name *dispersoid* to indicate heterogeneous systems in general.

Suppose that we imagine the case of a solid which has been coarsely powdered and suspended in water. If the particles are sufficiently large we shall be able to distinguish them with the eye or under the microscope. In that case, we have a suspension. It is clear that if we reduce the size of the separate particles of solid sufficiently we shall reach a stage when they are no longer visible, even with the aid of the microscope; at that point we reach the region of a colloidal solution. We can imagine the process of section carried further, until each particle of the disperse phase is a single molecule; and finally we may arrive at a stage where the degree of dispersion is such that the molecules are dissociated into ions. It will be seen from this that there is no possibility of drawing a sharp line between any two classes of colloids, for each type shades into the one next it by imperceptible degrees. The following rough classification is given by Wo. Ostwald.[1]



[1] Wo. Ostwald, *Grundriss der Kolloidchemie*, 1911, pp. 32–36.

* Specific superficies represents the total superficies divided by the total volume of the disperse phase.

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There is a further subdivision of colloid systems which we must take into account. An examination of various colloidal solutions shows that in practice they can be separated into two distinct classes: *suspensoids* and *emulsoids*. For example, when we determine the viscosity of two colloidal solutions, we may find that one of them has a viscosity practically identical with that of the solvent, while the other colloidal solution has a much greater internal friction. The former belongs to the class of suspensoids, while the latter is termed an emulsoid. Investigation has shown that temperature has a greater influence in the case of the emulsoids than in that of suspensoids. When we cool an emulsoid solution, the viscosity increases to a very marked degree as the temperature falls, while in the case of suspensoid solutions this phenomenon is not so prominent. A further difference between the two classes is observed in the phenomena of coagulation. The addition of a very slight trace of an electrolyte to a suspensoid will cause it to coagulate, but in the emulsoid group a much greater quantity of electrolyte is required before coagulation sets in.

Though, technically speaking, the subject of the colloids falls more within the province of physics than within that of chemistry, it has in practice become a chemical problem rather than a physical one. There are two reasons for this. On the one hand, the chemical side of the question comes to the front in the preparation of the substances; most recent research has been led up to by purely chemical investigations. Secondly, of late years organic chemistry has come more and more into touch with physiology; and in this way the importance of colloids has been brought home to both organic and physical chemists, since almost all the more complicated natural substances are colloidal in nature. It thus becomes of very considerable importance to us to gain some knowledge of the character and properties of this class of bodies.

In the following pages, a brief account will be given of the preparation and properties of the colloids, laying most stress upon the sol form; and some attempt will be made to indicate the more important hypotheses which have been put forward to account for the existence of this type of substances. At the same time, it must be remembered that only the most general treatment can be aimed at in the space at our disposal. A

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subject which now possesses a journal of its own can hardly be dealt with—except in the most cursory manner—within the limits of a single chapter.

2. The Preparation of Colloids

In this section we need not enter into any details as to the preparation of those organic substances of high molecular weight which occur naturally in animal and vegetable tissues. It will serve our purpose better to confine ourselves to much simpler cases which are known among inorganic compounds and elements, for in them the main characteristics can be more clearly seen than is the case with the more complicated organic bodies.

The first method of preparing colloids is by the ordinary process of double decomposition. Here, however, we must recognize two different types; for, as a result of our double decomposition, we may have formed in addition to our colloid a non-electrolyte or an electrolyte. Suppose we take an alkyl derivative of aluminium and add it to water; a hydrocarbon is produced, and the aluminium hydrate is precipitated in colloidal form—

$$2Al(CH_3)_3 + 6H_2O = Al_2(OH)_6 + 6CH_4$$

An examination of the right-hand side of the equation will show that in this case, apart from the colloid, we shall have nothing left in the solution, so that we can complete the isolation of the colloidal mass by simple filtration. On the other hand, we may precipitate aluminium from its salts by means of alkalis—

$$Al_2(SO_4)_3 + 6NH_4OH = Al_2(OH)_6 + 3(NH_4)_2SO_4$$

In this case we have left, along with the aluminium hydroxide gel, the ammonium sulphate formed in the reaction. To get rid of this we may adopt either of two methods. We may simply wash with water until we remove all ammonium sulphate, leaving behind on the filter the aluminium hydroxide. This method is rather tedious, and in some cases may not lead to a good result; for the colloid, when nearly freed from the ammonium salt, may go into solution as a hydrosol, and in this condition sink into the pores of the filter-paper. (This is

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often noticeable in ordinary analyses.) The second method of separating colloids from crystalline salts depends upon the fact that colloids pass through an animal membrane very slowly, though crystalloids do so with ease. This phenomenon was noticed by Graham, who gave to it the name *dialysis*. To separate the colloid from the crystalloid, we need only place the mixture of the two in a dialyzer, and add water. The water outside the dialyzer must, of course, be changed repeatedly, in order to promote rapid dialysis of the crystalloid. It should be noticed that even a sol will not pass through a dialyzer; so that even if we start with a mixture of ammonium sulphate and a colloid, both in solution, the dialyzer in the end will contain the colloid sol which it has retained, while the crystalloid ammonium sulphate will have passed out.

A second method of preparing colloids depends upon the hydrolysis of salts of metals. For example, if we boil a solution of aluminium acetate for a time, it breaks down into aluminium hydroxide and acetic acid; the latter, being volatile, disappears from the solution, leaving the colloid—

$$Al_2(C_2H_3O_2)_6 + 6H_2O = Al_2(OH)_6 + 6CH_3.COOH$$

Since the decomposition of the acetate is not likely to be complete, it is usually necessary to dialyze the solution in order to get rid of the undecomposed portion.

A third method of preparation rests upon the conversion of one colloid into another. For instance, if we act upon tin with nitric acid of specific gravity 1·35, we obtain metastannic acid. This body, if left long in contact with hydrochloric acid, becomes soluble in water, and gives stannic acid hydrosol. We have thus got a colloidal solution. If to this we add sulphuretted hydrogen, we shall convert the stannic acid into sulphide of tin, which is also a colloid. Thus we have prepared one colloid from the solution of another.

Bredig[1] has shown that many metals may be reduced to a colloidal condition by using wires of them as electrodes for a small arc which is allowed to play under water. In this way the metal is thrown off in such a finely divided condition that it forms a sol with the water.

A fifth method of preparing colloid sols is to liquefy a

[1] Bredig, *Anorganische Fermente*, 1901, pp. 22 ff.

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colloid gel. It is found that in some cases a mere trace of an electrolyte will convert a solid gel into a fluid sol. Graham[1] found that if one part of caustic soda in ten thousand of water were added to two hundred parts of silicic acid, and the whole was heated to 100° C. for an hour, the corresponding sol was produced.

Finally, under certain conditions, hydrosols of metals can be obtained by precipitating the metals from their solutions by means of reducing agents such as formaldehyde or hydrazine. This method has not a very wide field of application, however, as it is chiefly confined to the noble metals.

3. The Properties of Colloidal Solutions

Diffusion.—It has already been pointed out that a very striking difference between colloids and crystalloids is to be found in their relative capacity for diffusion through animal membranes. One or two examples will make clear the enormous difference in this respect between the two classes of bodies. The figures below show the relative intervals of time which elapse before the same amount of substance is dialyzed at a temperature of 10° C.

Colloids.		Crystalloids.	
White of egg	49	Hydrochloric acid	1
Caramel	98	Sodium chloride	2·33
		Magnesium sulphate	7
		Sugar	7

From this extreme slowness of diffusion we may deduce that the force driving the colloid molecule (its osmotic pressure) is extremely small, or that the friction of its passage through the solution is very great. It is very probable that both these factors play a part in the matter. Osmotic pressure measurements in colloid solutions show that the pressure is very small indeed, and the molecular weights of the colloids are probably of the order of 10,000. Sabanejeff and Alexandroff[2] found that white of egg has a molecular weight of about 14,000; and this is probably near the lower limit. But all these measurements depend upon the assumption that we are dealing with a true solution.

[1] Graham, *Ann. Physik.*, (2) 1864, 123, 529.

[2] Sabanejeff and Alexandroff, *J. Russ. Phys. Chem. Soc.*, 1898, [1], 7.

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Optical Properties.—When we go into a room which is lit by ordinary diffused light, we do not detect the dust-particles which are floating in the air about us; but if we go into a darkened room through which a strong ray of sunlight is allowed to pass, we see the whole beam of light filled with moving specks of light. A similar effect can be observed in the case of some fine particles suspended in a liquid. To the naked eye in diffused light, the beaker containing the liquid appears to contain no suspended material, but if we place the beaker in a dark room and pass a fine beam of light through the liquid, we see the suspended particles floating through the beam. If the particles are sufficiently fine, we shall not be able to detect them with the naked eye, but we shall merely see a bright bar where the ray passes through the liquid. Now, such a bar of light might be produced in either of two ways. If the substance in the beaker were a fluorescent body, it might be absorbing the rays of the beam and sending out other rays; whereas if we have a mere suspension, the light which we see is simply reflected from the surface of the particles. To distinguish between these two cases, we examine the emitted light with a Nicol prism, and if the light is polarized, it is clear that we are dealing with a suspension which reflects light from the surface of its particles and hence shows the ordinary phenomena of polarization by reflection; the light emitted by fluorescent solutions is not polarized, as it is produced by intramolecular vibrations of the solute, and not by reflection from the surface of the particles.

Upon this basis, the modern ultra-microscopic investigations have been built. The elements of the ultra-microscope are simple, though of course in actual practice there are many refinements which we need not describe here. The solution to be examined is placed in front of a dark background, and through the side of the vessel a very powerful beam of light is passed, usually concentrated to a focus in the middle of the liquid by means of a lens. An ordinary microscope is then focussed upon some part of the light ray, the axis of the microscope and that of the ray being inclined at right angles to one another. If the microscope be a low powered one and the suspension be very concentrated, it is probable that even with the aid of the microscope we shall not be able to see more

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than a bright haze in the field. But by diluting the suspension by degrees, we come to a point where separate particles become visible on the dark background, and finally on further dilution we reach a stage where the number of particles in the field can be counted at a glance. Thus if we know the mass of substance in the original suspension we can tell the mass of the body in the field at the last stage in the process, and on dividing this by the number of particles which we count in the field, we can form an estimate of the average size of the particles in the suspension. By means of the ultra-microscope it is possible to recognize the existence of particles having a linear diameter of $5\mu\mu$ ($1\mu\mu = 0{\cdot}000001$ mm.). From investigations with this instrument it appears that organic colloids are built up from larger and smaller masses, some of which are so small as to evade the ultra-microscope at times. Colloidal metals, on the other hand, appear to be formed of masses of small independent particles; and in the cases of several metals, it has been possible to measure (of course only very approximately) the linear dimensions of some of the particles. The following figures give some idea of the size of these objects.

Gold hydrosol	29—80μ
Platinum hydrosol	44μ
Silver hydrosol	50—77μ

In some gold hydrosols, particles having the linear dimensions $1{\cdot}7\mu$ exist; and since the diameter of a hydrogen molecule according to the kinetic theory is about $0{\cdot}00016\mu$, it follows that these particles have a diameter equal to ten thousand times that of a hydrogen molecule. In these hydrosols, therefore, we are reaching down very near to the confines of the molecular world.

Conductivity.—Turning now to the electrical properties of colloid solutions, we may deal first with the attempts which have been made to determine whether or not colloids are electrolytes. The results obtained by different investigators are somewhat contradictory. On the one hand, Billitzer,[1] Whitney and Blake,[2] from examinations of colloidal gold and platinum sols, came to the conclusion that the colloids had a distinct conductivity. For instance, Billitzer measured the

[1] Billitzer, *Wien. Ber.*, 1902, 111, 1393.
[2] Whitney and Blake, *J. Am. Chem. Soc.*, 1904, **26**, 1339.

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conductivity of water before and after the formation in it of colloidal platinum, and found the following figures—

Conductivity of the water	$0{\cdot}81 \times 10^{-6}$
Conductivity of the platinum hydrosol . .	$1{\cdot}14 \times 10^{-6}$.

Again, when a colloidal gold sol is placed in a dialyzer, it appears that the conductivity of the liquid within the cell is higher than that of the liquid outside.

On the other hand, it is suggested by some authors that the conductivity of sols is due to the presence of slight traces of electrolytes. Barus and Schneider [1] state that silver hydrosol is practically an insulator; Malfitano [2] observed that when a colloid was filtered through a collodion membrane a considerable part of it remained behind, and yet there was no change in conductivity produced by the filtration. Pauli [3] found that white of egg, after being purified by most careful dialysis, was almost a complete non-conductor.

The data at present known in this branch of the subject are evidently too few and too contradictory to allow us to form any definite opinion upon the question.

Cataphoresis.—The other electrical property which is of importance in the case of colloids is the phenomenon termed *cataphoresis.* If we take a porous cell, place it in a bath of some weak electrolyte, and then dip one electrode into the cell and another into the bath, we shall find, on switching on the current, that the water-level rises at one electrode and sinks at the other, provided the current be sufficiently strong. The explanation of the phenomenon is to be found in the fact that, by the passage of the current, the portions of the electrolyte which are lying in the narrow tubes formed by the porosity of the cell wall are propelled in the direction of the electric current (at least in aqueous solutions), and consequently the water-level rises in the cell containing the cathode. The phenomenon is analogous to osmosis, and is sometimes termed *electrical osmosis.* It has been observed that this electrical wandering takes place in the case of certain liquids in which particles are suspended; and from this it is only a step to fine

[1] Barus and Schneider, *Zeitsch. physikal. Chem.*, 1891, **8**, 278.

[2] Malfitano, *Compt. rend.*, 1904, **139**, 1221; but compare Duclaux, *ibid.*, 1905, **140**, 1468.

[3] Pauli, *Beiträge chem. Physiol. Path.*, 1906, **7**, 531.

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colloidal substances. Picton and Linder[1] showed that in the case of the latter bodies the same rule held good; the direction of the wandering is determined by the chemical nature of the colloid. A sol of arsenic sulphide, which is acid in character, moves towards the anode, while ferric hydroxide sol wanders towards the cathode.

From the work of Pauli it appears that if white of egg be submitted to a long-continued process of dialysis it shows no cataphoresis, and the colloid therefore carries no recognizable electric charge. But if we add to the solution a drop of acid, we get the cataphoresis phenomenon at once, and the particles wander with the positive current towards the cathode. On the other hand, if we add a drop of an alkaline solution to the colloid, an opaque white mass wanders towards the anode. In other words, colloids in themselves have no electrical charge; but in presence of acids or acid salts they acquire a positive one; while in presence of alkalis they become negatively charged.

The Brownian Movement.—The last general phenomena connected with colloids which we need mention in this place, is what is termed the *Brownian movement.* In 1828, Brown observed microscopically that if a number of fine particles were suspended in water, they became actuated by some force which led them to vibrate rapidly through small arcs about a mean position. Recent research upon colloids has shown that within them the Brownian movement is going on continually. Now, it is natural to assume that this rapid vibratory movement owes its origin to the action of forces such as heat or light, which may set up convection or other currents in the solutions in which the Brownian movement takes place, and in this way induce the movements of the particles. A recent investigation of Smoluchowsky, however, appears to have disproved this hypothesis. This author[2] finds that the Brownian movement is a general phenomenon if the particles have a maximum diameter of 0·004 mm. For particles of this size, the average velocity in water at 23° C. is 0·00038 cm. per second. Smoluchowsky found that the chemical nature of the particles has very little effect; but great influence is exerted by the medium

[1] Picton and Linder, *Trans.*, 1892, 61, 148.
[2] Smoluchowsky, *Ann. Physik.*, [4] 1906, 21, 756.

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in which they are suspended, its viscosity being the main factor in the problem. The motion appears to go on as long as the particles float in the liquid, for even after a year they still seem to move as freely as ever. Neither heat from an outside source nor light is necessary to bring about the motion.

A study of the Brownian movement has been made by Svedberg[1] in the following manner. If we pass a solution containing a series of particles through the field of an ultramicroscope at constant velocity, we should see each particle represented by a straight line of light if the particle went direct through the field. If, however, the particles are endowed with the Brownian motion, we shall get a wavy line instead of a straight one, and then we can measure the amount of divergence from the mean quite simply by means of a cinematograph camera or a slipping photographic plate. If we know the speed at which the particles are passing through the field, it is easy to calculate the path of the particle in its Brownian movement in one plane. From a study of various cases, Svedberg was enabled to put forward two general propositions with regard to the movement. In the first place, he finds that the amplitude of vibration is directly proportional to the period of vibration. In other words, the Brownian movement is a uniform one, and is not similar to the motion of a pendulum which moves fast at the bottom of its path, and slowly at either end. Secondly, the distance traversed by a particle in unit time is proportional to the viscosity of the dispersion medium.

Ramsay[2] regards the Brownian movement as due to the impacts of the molecules of the fluid upon the solid, suspended particles; so that the process resembles that which takes place in a radiometer. From experimental data he calculated that a particle weighing $2{\cdot}8 \times 10^{-12}$ grms. would have a velocity of $1{\cdot}4 \times 10^{-4}$ cms. per second. Now, the addition of a trace of an electrolyte to a sol causes a cessation of the Brownian movement. But we have already seen that the action of a trace of alkali, for instance, is sufficient to convert a solid gel into a fluid sol; in other words, the action of the electrolyte is to break down the larger aggregates of the gel. If we suppose that water itself is made up of a series of

[1] Svedberg, *Kolliod-Zeitschrift*, 1910, 7, 1.
[2] Ramsay, *Proc.*, 1892, 7, 17.

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molecular aggregates, these in their impacts against the solid suspended matter will have sufficient momentum to produce Brownian movements; but if by the addition of an electrolyte these comparatively large aggregations are broken down, the smaller masses which result from their decomposition will not have sufficient weight to affect the solid particles.

Independently of each other, Einstein[1] and Smoluchowsky[2] from theoretical physical assumptions have deduced a formula which expresses the kinetics of disperse systems extremely well, and which agrees closely with the results of Svedberg. The formula of Einstein is—

$$\Delta = \sqrt{K \cdot \frac{R \cdot T}{N} \cdot \frac{t}{\eta r}}$$

in which Δ is the mean path of a particle, K is a constant, R is the ordinary gas constant, T is the absolute temperature, N is the number of particles of a gramme-molecule of the disperse phase, t is the period of vibration, η the viscosity of the dispersion medium, and r the radius of the particles, assumed to be spherical.

Catalytic Action.—The foregoing paragraphs give an idea of the general characteristics of the colloids, but in conclusion it may be well to mention one particular case which is of considerable interest. Bredig,[3] in studying the properties of his platinum sols, discovered that they have a ferment-like action upon many substances. For example, a comparison of the actions of emulsin and a platinum sol upon hydrogen peroxide showed a remarkable similarity between the two catalysts. Again, just as ferments can be poisoned with hydrocyanic acid or other bodies, so the platinum sol loses its ferment-like action in presence of traces of such poisons.

4. Coagulation

It has already been mentioned that under certain conditions we can change a sol into a gel and *vice versâ*. When a gel is produced the process is termed coagulation.

There appear to be no general rules to guide us in an

[1] Einstein, *Ann. Physik.*, [4] 1905, 17, 549.
[2] Smoluchowsky, *Ann. Physik.*, [4] 1906, 21, 756.
[3] Bredig, *Anorganische Fermente*, 1901.

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attempt to classify the methods by which coagulation may be brought about. Some sols are converted into gels by heating, but this is by no means a general rule. Again, some sols are coagulated by the addition of electrolytes to them; but there are exceptions to this also. Inorganic colloids appear as a whole to be unaffected by the addition of non-electrolytes; but, on the other hand, an organic colloid such as is found in egg albumen can be precipitated by alcohol. It is clear from this that there is no use attempting to classify the coagulation phenomena from the point of view of the agents which are employed to bring about the action. There is, however, another mode of arranging the reactions which will serve as a rough guide. It is found that the conversion of some sols into gels is a reversible reaction, while in other cases the process can only be made to take place in one direction. We therefore divide coagulation phenomena into two classes: first, those in which coagulation is reversible; second, those in which it is an irreversible reaction. Between these two classes comes a third; for in some cases it is possible to get a reversible reaction under certain conditions, while if these conditions be exceeded the process becomes irreversible.

Let us take up first the irreversible processes. It has been found, in the case of precipitation reactions, that the action is practically irreversible. The study of this class of reaction has led to the discovery of two points which are of some importance. In the first place, it is found that in order to precipitate an inorganic gel from the sol condition, a certain minimum amount of an electrolyte is required. The amount of the electrolyte necessary depends upon its nature; but it is an invariable rule that if the amount of electrolyte present be under the minimum quantity it will not precipitate the gel, no matter how long the solution be left to stand. Again, if we treat a colloid like arsenic sulphide with various salts, we shall find that the power of coagulation of the salt depends upon the valency of the cations and is independent of that of the anions. If we take a basic colloid such as ferric hydroxide, the conditions are reversed; for here the valency of the anion is the predominating influence, while that of the cation ceases to be of any account. This has been expressed by Hardy somewhat as follows. The power of precipitation of a salt depends upon the

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valency of one of its ions. The predominant ion is either positive or negative according as the colloidal particles move with or against the current. The ion having the power of coagulation has always an electric charge opposite to that of the particles.

We must now turn to the case of organic colloids. Here the chief coagulating agent is heat. It has been found that under certain temperatures coagulation does not take place, so that we can speak of the coagulation-temperature of a colloid. We must not, however, assume that the coagulation will always take place at this temperature; for it has been shown that if we purify the colloid from electrolytes by means of dialysis, we can then heat it above the coagulation-temperature without any coagulation taking place.

We now come to the question of reversible coagulation. If we warm glue, we obtain a liquid which on cooling returns again to the gel condition. A solution of gelatine in water will show the same series of changes. We need not enter further into the matter here. There is, however, another class of such changes which offer a peculiarity in their behaviour. If we slowly evaporate the water from a sol of silicic acid at ordinary temperatures, we obtain a glassy mass from which we can obtain the sol once more by merely adding water to the solid. But if we remove the water completely from the gel by heating it, we shall find that it no longer shows any tendency to re-dissolve, and no sol can be prepared from it. Thus in this case we have an example of the intermediate class of colloidal bodies, viz. those which have either a reversible or an irreversible coagulation according to the conditions we employ.

5. Theories on the Nature of Colloids

When we examine the properties of colloids as a whole, there are two properties which must be accounted for by any theory which seeks to make clear the nature of colloidal substances. The first of these is the property of coagulation possessed by colloids; the second is the electrical effects which are manifested by colloidal bodies. In the following paragraphs a brief summary of various views on the subject will be given;

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for further information the reader must be referred to Wo. Ostwald's *Grundriss der Kolloidchemie*, as well as to the original papers of the authors mentioned.

If we consider the nature of the colloids from the broadest possible standpoint, it is clear that we may regard them as one of two types, for they must be either suspensions or solutions. The earliest theory on the subject was put forward by Graham,[1] who regarded the difference between colloid and crystalloid merely as one of the degree of aggregation. He assumed that crystalloid silicic acid was made up of a series of very small crystals, so when the silicic acid became colloidal, it simply meant that these tiny molecular crystals became associated together into larger masses which had colloidal properties. Coagulation, on this view, is simply a further step in the process; the colloidal masses in turn become associated with each other and so produce the coagulated colloid. This view, though it suffices to explain the coagulation phenomena well enough, does not really get us much further forward; and it quite fails to explain why some bodies are capable of forming colloidal masses while others have not this property.

Van Bemmelen takes up a rather more complex idea. If we have two substances X and Y, it is often possible by choosing the proper conditions to convert them into another pair of substances, x and y, where x is a solution of X in Y, and y is a solution of Y in X. For instance, if we gradually add phenol to some water in a beaker, we shall in the first place have a simple solution of phenol in water. If we continue to add phenol, however, until 8 per cent. of it is present, no more can be dissolved in the water, and any additional phenol which we add will sink to the bottom of the vessel and form a layer there. This layer of phenol, however, is capable of dissolving water; so that we have a solution of water in phenol at the bottom of the beaker instead of pure phenol. Thus our two starting substances, water and phenol, are now replaced by two other substances: a solution of phenol in water and a solution of water in phenol. If we raise the temperature of the beaker, we bring the solubility of phenol in water nearer to that of water in phenol; and eventually, at about 68° C., we reach a point at which the two are equal. At this

[1] Graham, *Annalen*, 1862, 121, 1.

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temperature the two liquid layers will become merged into each other and the liquid will be homogeneous. The presence of foreign substances will naturally affect the conditions of solubility and equilibrium, just as the temperature does.

Let us apply an analogous view to the case of a gel separating from its sol. Take the case of colloidal silicic acid as a concrete example. We have here the water as before, and instead of phenol we have silicic acid. These will form two different substances, the gel and the sol. Now, an examination of the structure of gels shows that they are really absorptions of the sol-liquid contained by membranes of semi-solid gel material. In other words, to some extent we have a solution of the gel in the sol to form a viscous material; and on the other hand we have a clear solution of the gel in the sol. Naturally, just as in the case of phenol in water, we shall have an equilibrium which is capable of being influenced by the presence of salts or by the variation of temperature. This view of colloid structure is remarkably interesting from some points of view.

The partition theory of Spiro and Hofmeister[1] depends upon somewhat similar conceptions. If we take as a basis the salting-out of ether from water by means of sodium chloride, we shall have a rough representation of the colloid coagulation according to the partition theory. Let us suppose that we have a colloid in solution, and that when we add alcohol to the solution we precipitate the colloid. We have then a system of two phases, each of which contains some of each of the three components: colloid, alcohol, and water. Since the alcohol will be evenly distributed through the water, it is clear that we have a constant relation between alcohol and water in the precipitated part of the colloid; but the relation of colloid to alcohol is not constant. The precipitated phase is obviously weaker in solvent than the original solution was; this has been shown to be the case with gelatine solutions, when a series of precipitations is carried out with salt solutions of gradually increasing concentration. Spiro finds, however, that this deprivation of solvent is not the only causal influence in the precipitation; for other properties of the precipitant, such as

[1] Hofmeister, *Arch. exp. Path. Pharm.*, 1890, **27**, 395; 1891, **28**, 210, Spiro, *Beiträge chem. Physiol. Path.*, 1903, **4**, 320.

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surface tension, compressibility, and viscosity, appear to enter into the problem as well.

In the foregoing theories, it will be observed, no particular attention is paid to the electrical properties of colloids. These properties, however, are so peculiar and so marked that several authors have based on them various views as to the nature of colloidal substances. We must now turn to examine these suggestions.

In one of the previous sections of this chapter, we have mentioned that the direction of the electric cataphoresis of colloids depends upon their nature; the acidic colloids wander towards the anode, while the basic colloids move in the direction of the cathode. Hardy [1] has shown that a similar phenomenon can be produced by adding an electrolyte to the colloid solution. It will be remembered that pure white of egg shows no cataphoric action whatever. But if we add to it a little alkali, we find that cataphoresis takes place, and that the particles of colloid move towards the anode; whereas if we electrolyze in acid solution, the colloid wanders to the cathode. We can best explain this by assuming that in alkaline solution the particles of colloid in white of egg are negatively charged, while in acid solution they are positively charged; the solution in each case being charged with electricity of opposite sign. If we have a neutral solution—*i.e.* in the case when we have the pure colloid present—there is practically no difference in potential between the particles and the liquid, so that both are "iso-electric." Now, on Hardy's view, the explanation of colloid phenomena is to be sought in this state of affairs. It will be remembered that in many cases the action of the precipitant depends upon the nature of its cation. In these cases, the colloid particles are negatively charged, and the addition of the precipitant discharges them and thus brings the whole system near the "iso-electric" point. As soon as this point is reached, the particles cease to interact electrically with the liquid around them and simply become influenced by gravity, with the result that they flock together and are precipitated.

Bredig [2] has put forward somewhat similar ideas, but in

[1] Hardy, *Zeitsch. physikal. Chem.*, 1900, **33**, 385.

[2] Bredig, *Anorganische Fermente*, p. 15.

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addition he points out that the removal of the charge would leave the surface tension free to produce a centripetal movement of the particles, and thus lead to coagulation. On this view, coagulation is caused by a capillary-electric surface diminution, which proceeds more rapidly the greater the surface tension of the suspension becomes with respect to the liquid, owing to the decrease of the potential difference and the simultaneous absorption which occurs.

Billitzer has criticized these views on the ground that absence of potential differences cannot be the sole cause of coagulation; for that phenomenon can be brought about in the case of colloidal platinum by means of alcohol, formaldehyde, or even by salts which are not hydrolytically dissociated, such as potassium chloride. Again, if we examine the potential of mercury in conjunction with its surface tension, we find that the surface tension reaches its maximum when there is a difference of potential of three-quarters of a volt between the metal surface and the liquid. If the theory were correct, the maximum surface tension should coincide with the minimum potential difference.

Billitzer's own explanation[1] is somewhat as follows. In the solution of an electrolyte the colloid particles which are charged positively with respect to the liquid draw to themselves the anions, which they condense upon their surfaces; negatively charged particles attract the cations in a similar manner. In this way the ions act as condensation germs by attracting the charged particles and producing a large uncharged mass. The process is somewhat similar to that which takes place in the ordinary "dust-counter," in which each dust-particle serves as a nucleus around which water-vapour condenses. It has been proved by Linder and Picton[2] that colloidal arsenic sulphide absorbs barium ions from barium chloride solution; and similar results have been obtained by Whitney and Ober[3] and by Spring.[4] Billitzer has shown that

[1] Billitzer, *Zeitsch. Electrochem.*, 1902, **8**, 638; *Wien. Ber.*, 1902, **111**, 1393; 1903, **112**, 95; 1904, **113**, 1159; *Zeitsch. physikal. Chem.*, 1903, **45**, 307; 1904, **51**, 129.

[2] Linder and Picton, *Trans.*, 1895, **67**, 63.

[3] Whitney and Ober, *J. Amer. Chem. Soc.*, 1902, **23**, 842.

[4] Spring, *Arch. sc. phys. nat.*, (4) **10**, 305.

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this absorption takes place *during* the coagulation process, which certainly strengthens his theory.

Another view of colloids has been put forward by Donnan.[1] He considers what would happen if a substance had a negative surface tension. Under these circumstances, it would cease to exist in its first form and pass into a second condition of division. At some particular point in the process we reach a state in which the potential energy of the system is at a minimum. At this point the particles of the body reach what may be called a critical size in grain. The critical grain size can be reached either by the breakdown of larger agglomerations or by the union of finer particles. For instance, if we have a large agglomeration in the liquid, it will be acted upon by two forces; on the one hand we have the attraction from the centre of the mass of particles, and on the other hand we have the pull of the particles of solvent from the outside. These two mutually opposed forces will come into equilibrium when the agglomeration is reduced to the critical size of grain. At this point we have a colloidal solution.

There are many other theories of the nature of colloids, but into these we cannot enter here. It is supposed by some authors[2] that colloidal solutions are produced by the formation of chemical complexes; other views demand the hypothesis that there are two kinds of molecules.[3] Enough has been said to show the nature of the problem before us.

[1] Donnan, *Phil. Mag.*, (6) 1901, 1, 647; *Zeitsch. physikal. Chem.*, 1901, **37**, 735; 1903, **46**, 197.

[2] See *Bull. Soc. chim.*, 1899, **21**, 137; *J. Chim. phys.* 1907, **5**, 29; *Zeit. anorgan. Chem.*, 1903, **35**, 16.

[3] *Zeitsch. physikal. Chem.*, 1902, **39**, 468.

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CHAPTER VI

REACTIONS IN LIQUID AMMONIA

1. The Properties of Liquid Ammonia

Liquid ammonia is a colourless, mobile substance of boiling-point approximately −38° C., and a density about 0·6 that of water. At −77° C. it solidifies to white transparent crystals.

When we compare the properties of this body with water, we can find many analogies between the two substances. The boiling-point of ammonia is considerably lower than that of water, but lies much nearer to it than do those of such substances as methane, hydrogen sulphide, or hydrochloric acid. On the other hand, the specific heat of liquid ammonia and the heat of fusion of the solid substance are greater than the corresponding constants of water and ice. The dielectric constant of liquid ammonia is about 20, which is sufficiently high to indicate that it is probably associated, like water. Its critical temperature is also comparatively high; and its critical pressure is the highest known with the exception of that of water. Its boiling-point elevation constant[1] is the lowest yet observed, being 3·4 as compared with the 5·2 of water. In the table below are some figures[2] which serve to show to what extent the two substances resemble each other:—

	Liquid ammonia.	Water.
Melting-point . . .	−77°	0°
Boiling-point . . .	−38°·5	+100°
Specific gravity at 0° C. .	0·6234	1
Critical temperature . .	+131°	+365°
Critical pressure . .	113 atmospheres	200·5 atmospheres

Liquid ammonia has the power of dissolving many substances. Salts are not so readily soluble in it as they are in

[1] Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 277; **24**, 83: *J. Amer. Chem. Soc.*, 1905, **27**, 191.

[2] Roscoe and Schorlemmer, *Treatise on Chemistry*, 1905, I.

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water, but, on the other hand, it has a much greater power of dissolving carbon compounds than water shows. Further, it is a good ionizing medium; dilute solutions of substances in liquid ammonia are often better conductors than aqueous solutions of the same strength.

2. Reactions between Inorganic Salts, Bases, and Acids in Liquid Ammonia Solutions

The first worker who directed attention to the fact that liquid ammonia might be utilized as a solvent appears to have been Gore,[1] who in 1872 carried out some experiments in this direction. In recent years Franklin[2] and his co-workers have dealt very fully with this problem, and we shall devote the present chapter to an account of the results arrived at by them.

In the first place, however, we must deal with the classification of the salts which has been proposed by Franklin.[3] He takes as his starting-point the parallelism between water, oxygen bases, and oxygen acids on the one hand, and ammonia, metallic amides, and acid amides on the other. The oxygenated bodies he terms hydro-salts, hydro-bases, and hydro-acids; while the corresponding ammonia derivatives are named ammono-salts, ammono-bases, and ammono-acids. Thus potassium nitrate is a hydro-salt; sodium hydroxide is a hydro-base; and acetic acid is a hydro-acid. Potassium acetamide, sodium succinimide, and sulphamide are ammono-salts; sodamide, lead imide, and mercuric nitride are ammono-bases; while acetamide, carbamide, and succinimide are ammono-acids.

We shall examine in the present section the reactions between some hydro-salts in ammonia solution; and in the later sections shall deal with the behaviour of the ammono-class, which differs to some extent from that of the oxygen compounds.

It was shown by Franklin and Kraus[4] that when two inorganic salts are dissolved in liquid ammonia, the reaction

[1] Gore, *Proc. Roy. Soc.*, 1872, **20**, 441; 1873, **21**, 140.
[2] See Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.
[3] *Ibid.*
[4] Franklin and Kraus, *Amer. Chem. J.*, 1899, **23**, 83.

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between them may not follow the same course as it does in aqueous solution. The reason for this is, of course, the fact that the solubility of salts is not the same in ammonia as in water. For instance, if we mix sodium chloride with calcium nitrate in aqueous solution, no precipitation occurs; but if we repeat the experiment in ammonia solution we shall obtain a precipitate of calcium chloride, a result which could not possibly be obtained in aqueous solution.

As far as is known at present, metallic hydroxides are insoluble in liquid ammonia. On the other hand, when acids are brought into contact with that substance they first unite with it to give ammonium salts, and the latter bodies are soluble, giving *acid* solutions. It should be noted that liquid ammonia is not a basic substance; so that when an acid is dissolved in it, the solution thus obtained has acid properties. This can be shown in the following way. Phenolphthalein is dissolved in liquid ammonia, and is coloured by the addition of a trace of alkaline hydroxide. On adding an acid to the ammonia, the colour is discharged, though of course there is a very large excess of liquid ammonia present.

Again, just as a dilute solution of ammonium sulphate in water will dissolve magnesium, so a solution of an ammonium salt in liquid ammonia will dissolve sodium or magnesium, hydrogen being evolved in this case also. The equation of the reaction in the case of sodium and ammonium chloride would be—

$$2Na + 2NH_4Cl = 2NaCl + 2NH_3 + H_2$$

Further, Divers had shown that such substances as sodium hydroxide were soluble in solutions of ammonium nitrate, though they are not soluble in liquid ammonia. Franklin[1] examined cases of ammonium salts other than the nitrate, and found that the property is a general one. It thus appears that bases dissolve in solutions of ammonium salts in ammonia in a manner exactly analogous to the solution in acids of bases which are insoluble in water. Thus, as Franklin points out, the action must follow the course indicated below:—

$$NaOH + NH_4Cl = NaCl + H_2O + NH_3$$
$$CaO + 2NH_4NO_3 = Ca(NO_3)_2 + H_2O + 2NH_3$$

[1] See Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

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We need not enter further into the description of this part of the subject. In the following section we shall deal with the reactions of the ammono-salts and acids.

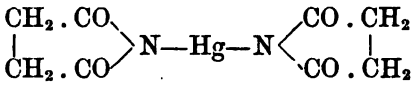
3. The Reactions of Ammono-salts, Ammono-bases, and Ammono-acids in Liquid Ammonia Solution

If we dissolve some phenolphthalein in liquid ammonia, it is coloured red when a metal amide is added to the solution but the colour can be discharged by the addition of an acid amide. Thus if sodamide be allowed to react with acetamide in liquid ammonia, we shall obtain an ammono-salt, sodium acetamide, in accordance with the following equations:—

$$CH_3.CO.NH_2 + NaNH_2 = CH_3.CO.NHNa + NH_3$$
$$CH_3.CO.NH_2 + 2NaNH_2 = CH_3.CO.NNa_2 + 2NH_3$$

These reactions have been studied by Franklin and Stafford.[1]

By analogy with the hydro-salts in aqueous solution,[2] these ammono-salts ought to be good electrolytes. Franklin and Kraus have tested this view in the case of mercury succinimide—



and have found it to be correct.

It will be remembered that some metallic hydroxides behave as if they were slightly acidic. For example, aluminium hydroxide dissolves in a solution of caustic potash, giving potassium aluminate. A similar class of substances has been discovered among the ammonia-series, for some metallic derivatives of ammonia, such as the silver, lead, and aluminium compounds, dissolve in excess of potassamide solution.

Among the ammono-bases we class such substances as metallic amides, imides, or nitrides. These compounds dissolve in liquid ammonia exactly in the same way as metallic hydroxides dissolve in water. Potassamide is especially soluble in ammonia; and in consequence of this property, Franklin[3] has utilized that substance in the preparation of a number of

[1] Franklin and Stafford, *Amer. Chem. J.*, 1902, **28**, 13.
[2] Franklin and Kraus, *J. Amer. Chem Soc.*, 1905, **27**, 191.
[3] See Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

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insoluble metallic derivatives of ammonia by simply bringing together a soluble metallic salt and potassamide in ammonia solution. The double decomposition takes place in a way perfectly analogous to that which occurs in aqueous solution, and the required body is obtained as a precipitate—

$$AgNO_3 + NH_2K = AgNH_2 + KNO_3$$
$$Pb2NO_3 + 2NH_2K = NHPb + 2KNO_3 + NH_3$$
$$3HgI_2 + 6NH_2K = N_2Hg_3 + 6KI + 4NH_3$$

The soluble metallic amides form solutions which are good electrolytes.

The ammono-acid group of substances includes a somewhat varied assortment of compounds. We have already mentioned some acid amides, and to these we must add acid imides. Further, while the nitrides of metallic elements act as bases, it has been found that the non-metallic nitrides yield acids with liquid ammonia; so that here the parallel between hydro-bodies and ammono-compounds is very close. Again, since the halogen derivatives of strongly electro-negative elements, such as phosphorus, are hydrolyzed by water, they are attacked also by liquid ammonia, giving rise to substances analogous to the water hydrolysis products, hydroxyl being replaced by the ammonia group. The following equations will make the matter clear:—

$$PCl_3 + 5NH_3 = NH : P . NH_2 + 3NH_4Cl$$
$$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl$$
$$B_2S_3 + 6NH_3 = B_2(NH)_3 + 3NH_4SH$$
$$SiSBr_2 + 4NH_3 = SiS(NH_2)_2 + 4NH_4Br$$

Picramide must also be included in this category. It is the ammono-analogue of picric acid—

$HO . C_6H_2(NO_2)_3$	$NH_2 . C_6H_2(NO_2)_3$
Picric acid	Picramide

4. Ammonolysis

From the foregoing sections it will have become clear that the reactions which take place in liquid ammonia are closely allied to those with which we deal in aqueous solution.

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Franklin[1] therefore proposes to term them *ammonolytic reactions* in order to recall their close resemblance to hydrolytic ones. Further, since we find reversible reactions among the hydrolytic class, we should expect to find something of the same nature amongst ammonolytic reactions. Research has shown that this is actually the case.[2] When mercuric chloride, mercuric iodide, and lead iodide are treated with liquid ammonia, the following reversible equations represent their behaviour:—

$$HgCl_2 + 2NH_3 \rightleftharpoons NH_2HgCl + NH_4Cl$$
$$2HgI_2 + 4NH_3 \rightleftharpoons HgNHgI + 3NH_4I$$
$$2PbI_2 + 6NH_3 \rightleftharpoons Pb(NH_2)_2 . NH_2PbI + 3NH_4I$$

In these cases the ammono-basic salts NH_2HgCl, Hg_2NI, and $Pb(NH_2)_2 . NH_2PbI$, appear as solid phases, while the remaining components of the system constitute the liquid phase.

Thus, parallel to hydrolysis in aqueous solution, we have in liquid ammonia solution a process of *ammonolysis* going on.

5. Other Ionizing Media

The power of dissociating dissolved salts is not confined to water and ammonia, but has been observed among the most varied types of compounds, both organic and inorganic. Alcohols, amines, alkyl thiocyanates, nitriles, liquid sulphur dioxide, arsenic halides, and phosphorus oxychloride are all capable of furnishing conducting solutions when salts are dissolved in them. A very considerable mass of detailed information has been acquired in this department of the subject during the last five or six years; but at the present time many of the data are contradictory, and it is hardly possible to draw any certain conclusions. The work of Walden and others may be consulted on the point.[3]

[1] See Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

[2] Franklin and Cady, *J. Amer. Chem. Soc.*, 1904, **26**, 499.

[3] Carrara, *Gazzetta*, 1903, **33**, I. 241; Centnerszwer, *Zeit. physikal. Chem.*, 1901, **39**, 220; Dutoit and Levier, *J. chim. phys.*, 1905, **3**, 435; Jones and Lindsay, *Amer. Chem. J.*, 1902, **28**, 329; Jones and Carroll, *ibid.*, 1904, **32**, 521; Kahlenberg, *Zeit. physikal. Chem.*, 1903, **46**, 64; Kahlenberg and Schlundt, *J. Physical Chem.*, 1902, **6**, 447; Kahlenberg and Ruhoff, *ibid.*, 1903, **7**, 254; Mathews, *J. Physical Chem.*, 1905, **9**, 641; Schlundt, *ibid.*, 1901, **5**, 157; Walden and Centnerszwer, *Zeit. physikal. Chem.*, 1901, **39**, 513; *Zeit. anorgan. Chem.*, 1902, **30**, 145; Walden, *Zeit. physikal. Chem.*,

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We may confine ourselves here to the results which have been obtained by Walden in the course of his researches upon the influence of various media upon dissolved substances. The method employed by him was to use a standard electrolyte of such a character as to be soluble in all the liquids which he intended to examine. This substance he found in tetraethyl ammonium iodide. The conductivities of solutions of this body were then examined, and compared with the various physical properties of the solvent with a view to detecting any parallelism. The chief results were as follows.

In general, the equivalent conductivity of a solution increases on dilution, just as is the case with aqueous solutions; but in several cases there are irregular variations which may be due to some action between the solute and the solvent. There appears to be no connection between the equivalent conductivity and the associating power of the solvent; nor is there any apparent relation between the conductivity and the dissociating power of the solvent employed. There appears to be little connection between the value of the equivalent conductivity and that of the dielectric constant; and no conclusion with regard to the degree of dissociation can be drawn from the measurement of the conductivity. Walden has found that there is a close relation between the viscosity and the limiting value of the conductivity; this relation is independent of the temperature and the nature of the solvent employed, and can be expressed by the equation—

$$\Lambda_{\infty}^{0^\circ} \times \eta_{\infty}^{0^\circ} = \Lambda_{\infty}^{25^\circ} \times \eta_{\infty}^{25^\circ} = 0{\cdot}7$$

By means of this we can determine the limiting conductivity if we know the value of the viscosity of any liquid. Further, the product of the equivalent conductivity and the temperature-coefficient of conductivity is approximately constant—

$$\Lambda_{\infty} \times \text{temperature coefficient} = 1{\cdot}3$$

With regard to the influence of the chemical constitution of the solvent upon the conductivity, Walden has found that

1900, **25**, 371; 1908, **43**, 385, **46**, 103; 1905, **54**, 129; 1906, **55**, 207, 281, 683; *Zeit. Electrochem.*, 1905, **12**, 77; Baur, *Zeit. Electrochem.*, 1906, **12**, 725; Jones, Bingham and McMaster, *Zeit. physikal. Chem.*, 1906, **57**, 193, 257; Jones, Lindsay, and Carroll, *ibid.*, **56**, 129.

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solutions in which the higher members of a homologous series are employed as solvents have lower equivalent conductivities at infinite dilution than are found when the lower members of the series are used as solvents. Again, if we take an aromatic and an aliphatic substance of similar chemical nature (acetaldehyde and benzaldehyde, for instance), it is found that a solute in the aromatic body will give a lower equivalent conductivity than it would were it dissolved in the aliphatic solvent. Media containing ketonic, aldehydic, or cyanide radicles show the highest values of Λ_∞; while the lowest values observed were found in the case of bodies containing the amino or carboxyl radicles.

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CHAPTER VII

THE FIXATION OF NITROGEN

1. The Circulation of Nitrogen in Nature

Animals have two fundamental needs: oxygen and nourishment. Oxygen they can derive direct from the air, but nourishment can only be obtained by a more roundabout process. At the basis of all animal structure lies a group of substances called proteins, which the animal, being unable to synthesize itself, obtains from vegetables. These proteins contain from fifteen to twenty per cent. of nitrogen. It has been shown that non-nitrogenous vegetable products, such as sugars, are incapable of supporting life. Animals, therefore, subsist upon the nitrogenous bodies of the vegetable kingdom; but this only carries us a step further back, and leaves us to discover how this nitrogenous matter is obtained by plants. It is found that part of the nitrogen in plants is derived from the air by means of certain bacteria, but the major part of it comes from the decomposition of plant tissue by one means or another. For example, a plant may be eaten by an animal; a certain amount of the nitrogen is excreted in the form of urea derivatives and the like; these break down to ammonia, which is then oxidized by bacteria to nitrous and nitric acid; and these, in turn, are absorbed by the vegetable world once more.

If one could enclose a few plants and a suitable series of animals in a bell-jar, this process of nitrogen circulation might conceivably be prolonged indefinitely; but, unfortunately, when we have to deal with the matter from a practical standpoint, the question of waste bulks very largely. The scheme below shows the main steps in the process of circulation, and we have now to consider at what points waste is to be expected.

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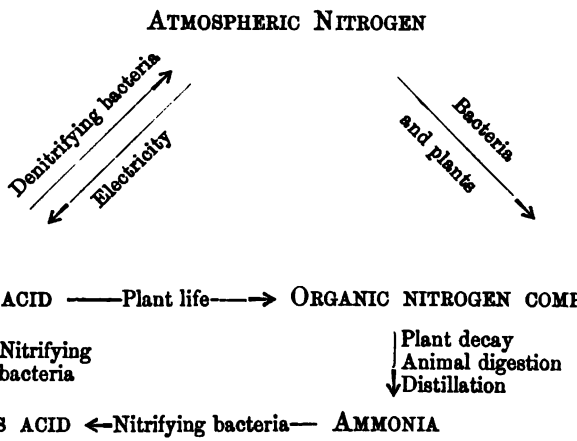

In the first place, we must bear in mind that though the vegetable kingdom as a whole has its uses in the question of respiration, where it counterbalances the loss of oxygen due to the animal kingdom, it is only certain groups of plants which can serve as food. Thus any nitrogen which is absorbed by non-edible plants is, temporarily at least, lost from the point of view of nourishment. Again, we dispose of the greater part of our sewage by running it into the sea; but in this way the larger portion of the nitrogen contained in it is lost to us and goes to build up sea-plants, for which we have at present no use. Further, the nitrous and nitric acids produced from ammonia in nature do not necessarily remain on the spot where they are produced; they may disperse and be lost, as far as practical purposes are concerned.

In the past, these losses have been counterbalanced by two methods: either by inoculating plants with nitrifying bacteria, or by manuring the soil in which they grow. With the former method we have no concern here, but we must enter into some consideration of the second.

At the present day, the nitre beds of Chili supply the major part of the demand for cheap nitrogenous matter which can be used in agriculture. Guye[1] gives the following figures, which show how great is the current consumption of nitrates. "In 1905, the entire consumption of Chili nitrate was 1,567,000

[1] Guye, *J. Soc. Chem. Ind.*, 1906, **25**, 567.

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tons; while that of 1896 was 1,060,000 tons. Of these 1,567,000 tons we can reckon about 300,000 tons as having been utilized in chemical industry. . . . The use of nitrate of soda as manure is represented by the balance, approximately, 1,267,000 tons for 1905; and this consumption is rapidly increasing, especially since a commencement has been made in the direction of applying nitrogenous manures to the culture of corn in the United States. Recent calculations by M. Vergara, which have taken into account the increase in the consumption of the last few years, indicate the year 1923 as the date when the Chili beds will be exhausted." In less than a generation, if these calculations be true, we shall be faced with the problem of producing nitrogenous substances upon a vast scale and at a reasonably low cost. By adopting a less wasteful method of sewage disposal, and perhaps by utilizing as nitrogen sources such substances as seaweed from the Sargasso Sea, we may hope to diminish the amount of synthetic material required; but at the best we cannot hope to dispense with it altogether.

Now, for synthetic purposes, the cheapest source of nitrogen is the atmosphere; and in the last few years many attempts have been made to tap this store by converting atmospheric nitrogen into some nitrogenous compound which can be used as a manure. This process has been termed the *fixation* of nitrogen. In the following sections of this chapter we shall deal with a few of the methods which have been devised with this end in view.

2. The Production of Nitrogen Oxides, Nitrous and Nitric Acids

In any technical process we must bear in mind two things which govern the price of the final product: the cost of the starting materials, and the expenditure of energy necessary to convert them into the compound required. Now, in the manufacture of nitrogen compounds, the cheapest source of nitrogen is certainly the atmosphere: but we have not only to obtain nitrogen; we have also to find some comparatively cheap substance with which to combine it; and, finally, we must devise an economical method of effecting the combination.

It is obvious that oxygen is the cheapest element we could

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choose in order to form a compound with nitrogen, for the two occur together in the atmosphere in what is, for practical purposes, an unlimited quantity. The question then arises, Can we convert nitrogen into its oxides with an expenditure of energy low enough to make it pay in practice? Up to the present time, the methods applied to this question have been almost entirely electrical; so that the problem, in this department at least, rests chiefly upon the cost of electricity.

Half a century ago, Berthelot pointed out that there were four chief modes of applying electricity to chemical problems: we may utilize—

1. The spark discharge.
2. The silent discharge.
3. The electric arc.
4. Electrolytic action.

Previous to this, Madame Lefebre[1] had patented a method of manufacturing nitric acid by means of sparking a mixture of air and oxygen; but her process does not seem to have met with much technical success. In 1863, Meissner[2] pointed out that if the gases used were made moist, the yield of nitrogen oxides was much increased. In 1882, Prim[3] showed that compression of the gases made a considerable improvement in the results obtained; and he detected, further, that much loss might be caused by using too strong a draught in driving the air through the apparatus and thus blowing out the spark. The subject has been very fully investigated by Muthmann and Hofer,[4] as well as by von Lepel[5] and by Rayleigh.[6] We need not enter into any further detail, as other processes have proved more practical than the spark discharge, and with these we must now deal.

Prim, in his investigations, had used a combination of the spark discharge and silent discharge, allowing them to act simultaneously upon a mixture of nitrogen and oxygen.

[1] Lefebre, English Patent, No. 1045 (1859).
[2] Meissner, *Ueber den Sauerstoff*, 1868.
[3] Prim, German Patent, No. 20,722.
[4] Muthmann and Hofer, *Ber.*, 1903, **36**, 438.
[5] Von Lepel, *Die Bindung des Atmosphärischen Stickstoffs*, 1903.
[6] Rayleigh, *Trans.*, 1897, **71**, 181.

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Siemens and Halske,[1] in their process, have omitted the spark discharge entirely. According to their view, the mechanism of the oxidation depends upon the formation of ozone, which, in breaking down into oxygen, becomes active enough to attack the nitrogen with which it is mixed. As is to be expected, the air must be kept dry when this process is employed, for otherwise the silent discharge would be without effect. Siemens and Halske found that when the process was applied to a mixture of oxygen and nitrogen, the yields were too small to make it of any practical value; but if ammonia gas were mixed with the air before it passed through the apparatus, solid ammonium nitrate was deposited on the walls of the vessels: and with this modification the method becomes possible from the technical point of view.

The third method of applying electricity to the problem, in which the electric arc is employed, has proved more satisfactory than the two which we have just described. Crookes,[2] in 1892, showed that at a temperature of a high tension arc, oxygen and nitrogen combined to form nitric oxide. Rayleigh [3] five years later proved that in this way 25 c.c. of oxides of nitrogen could be produced by the expenditure of one watt-hour. The action of the arc appears to be due purely to its heating effect; for McDougall and Howles,[4] as well as Muthmann and Hofer,[5] made it clear that the efficiency of the arc depended upon its temperature.

At this point it may be well to recall the work of Nernst [6] upon gas equilibria at high temperatures. If we take the case of the union of nitrogen and oxygen to form nitric oxide, we have the following equation:—

$$N_2 + O_2 = 2NO$$

An examination of this equation will show that the volume of gas at the beginning of the reaction is the same as that at the end. Now, if no change in volume takes place during a reaction, it is clear that the position of equilibrium of such a

[1] Siemens and Halske, German Patent, No. 85,103.
[2] Crookes, *Chem. News*, 1892, **65**, 301.
[3] Rayleigh, *Trans.*, 1897, **71**, 181.
[4] McDougall and Howles, *Mem. Manchester Phil. Soc.*, 1900, **4**, 44.
[5] Muthmann and Hofer, *Ber.*, 1903, **36**, 438.
[6] Nernst, *Application of Thermodynamics to Chemistry*, 1907.

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reaction would be uninfluenced by the pressure under which it is carried out. If we were to take a case in which an increase in gas volume occurred during a reaction, then pressure could exert an influence, for the newly formed gas would have to exert a pressure upon the rest of the gas in the containing vessel in order to make room for itself. No such pressure is required in the present case, so the reaction is not influenced by the external pressure.

The equation which we have written down above is not strictly accurate; instead of the sign of equality, we should have inserted the sign of a reversible reaction, for this reaction is actually a reversible one:

$$N_2 + O_2 \rightleftharpoons 2NO$$

Now, it is clear that the position of equilibrium in a reversible reaction is very largely dependent upon the temperature at which the reaction is carried out. Nernst has shown, for instance, that if air be passed through a tube heated to 1538° C., only 0·4 per cent. of nitric oxide was formed; while at 1922° C. the quantity rose to 1 per cent. The results appear to be in contradiction to the fact that nitric oxide decomposes at a white heat. The matter will be made clear if we take into account the velocities with which the two reactions—

$$N_2 + O_2 = 2NO \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$2NO = N_2 + O_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

take place. According to the Guldberg-Waage Law of Mass Action, the amount of chemical action is proportional to the active masses of the substances reacting. Thus the chemical action corresponding to equation (1) will be proportional to the amounts of nitrogen and oxygen present; while equation (2) represents an action which will be proportional to the amount of nitric oxide used. Thus if v_1 be the velocity of formation of nitric oxide, than we have the equation—

$$v_1 = k_1 \times (N_2) \times (O_2)$$

where (N_2) and (O_2) are the active masses of nitrogen and oxygen present. Again, if v_2 be the velocity of formation of nitrogen and oxygen from nitric acid, then—

$$v_2 = k_2 \times (NO) \times (NO) = k_2 \times (NO)^2$$

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Suppose, now, that the two reactions have proceeded until equilibrium has been reached. At this point, the amount of nitric oxide formed is equal to that decomposed. Consequently—

$$v_1 = v_2$$

and the equilibrium constant, K, is the ratio of the one velocity constant to the other. In other words—

$$K = \frac{k_2}{k_1}$$

Now, the values of k_1 and k_2 can be ascertained experimentally, so that we can easily determine the value of the equilibrium constant K.

When we apply this line of argument to the concrete case of the production of nitric oxide from the air, we proceed as follows. It is evident that the equilibrium constant K will be dependent upon the active masses of the three gases present, nitrogen, oxygen, and nitric oxide, and will be expressed thus—

$$K = \frac{(NO)^2}{(N_2) \times (O_2)}$$

Let x be the amount of nitric oxide produced at the equilibrium point; then, since the concentration of nitrogen at the start is 79 per cent., and that of oxygen is 21 per cent. (these being the proportions in which these gases occur in air), we have at constant temperature the following equation:—

$$K = \frac{x^2}{\left(79 - \frac{x}{2}\right)\left(21 - \frac{x}{2}\right)}$$

Since we can determine K experimentally, we can solve the equation for x, and this will give us the quantity of nitric oxide formed when the equilibrium point is reached.

Now, K alters with the temperature according to the equation—

$$\frac{d \log_e K}{dT} = - \frac{Q}{2T^2}$$

where Q is the change of energy in the system, and T the absolute temperature. Integrating this under the assumption

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that Q is independent of the temperature (as it apparently is for all practical purposes in the case we are considering), we then have for two temperatures T_0 and T_1 the equation—

$$\log_e K_1 - \log_e K_0 = \frac{Q}{2}\left(\frac{1}{T_1} - \frac{1}{T_0}\right)$$

Thus, if we know the equilibrium constant K_0 for temperature T_0, and also the energy change in the system, we can calculate from this last equation what the equilibrium constant will be for any other temperature T_1. The energy change in the system can be determined by finding the equilibrium constant for two temperatures, and then substituting in the above equation. In this way, from a couple of measurements at different temperatures, we shall be in a position to foretell the equilibrium constant of the reactions for any temperature. The agreement between theory and experiment is quite close, as the following figures [1] show :—

Temperature.	% NO observed.	% NO calculated.
1811°	0·37	0·35
1877°	0·42	0·43
2083°	0·64	0·67
2195°	0·97	0·98
2580°	2·05	2·02
2675°	2·23	2·35

Another point of importance arises in this connection. From what has already been said, it is clear that the velocity of decomposition of nitric oxide is very greatly influenced by the temperature at which the reaction is carried out. If we can bring the reactions into equilibrium at a temperature of about 2500° C., we shall have in the mixture, according to Nernst's data, about two per cent. of nitric oxide. If we cool the gases down slowly, they will come into a fresh state of equilibrium for each temperature they pass through, and consequently when we reach ordinary temperatures the percentage of nitric oxide will be negligible. On the other hand, if we produce a sudden drop in the temperature, the gases will not attain equilibrium quickly enough to keep pace with the fall in temperature, and consequently we shall be able to reach ordinary temperatures before the nitric oxide has time to decompose.

[1] Nernst, *Application of Thermodynamics to Chemistry*, p. 35.

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Once the ordinary temperature is attained, the decomposition of nitric oxide will proceed with such slowness as to be negligible from the practical point of view. Thus, if we could cool the mixture of gases instantaneously from 2500° C. to zero, we should preserve the two per cent. of nitric oxide which it contains at the higher temperature. Of course, in practice such instantaneous cooling is impossible; but if the gases be removed rapidly from the neighbourhood of the source of heat, it is possible to stave off the decomposition of the nitric oxide to a certain extent.

In the McDougall and Howles process, in which the mixture of oxygen and nitrogen is passed over the electric arc, the arc was kept stationary, and the cooling was achieved by using a rapid stream of gas, so that the oxides were swept along in the current and carried away from the arc as quickly as possible. An improvement[1] upon this was devised by Birkeland and Eyde, whose process has been utilized on a commercial scale at Nottoden, in Norway. In this process advantage is taken of the effect which a strong electro-magnet exerts upon arcs. If we fix opposite the middle of an electric arc a strong electro-magnet, the arc will be diverted and finally broken; after which it will reform between the electrodes, be diverted and broken again. By this means we replace the simple arc by a series of arcs, which form, bend outwards, and break. If the apparatus be properly adjusted, it is possible by this means to produce an arc in the form of a thin disc instead of the usual narrow stream. The advantages of the Birkeland and Eyde method are twofold: in the first place, since the disc of the arc is very thin, a gas passing through it is only heated for a very brief interval; secondly, owing to the increase in diameter of the arc, it is possible to pass a much larger quantity of gas through it than is the case when the gases are passed across an ordinary arc. After the gases have been passed through the arc they are conducted into a cooling apparatus; they are next led into an oxidizing chamber, where the nitric oxide becomes nitric peroxide. The final product of the process is basic calcium nitrate; the basic salt is prepared in preference to the normal nitrate, owing to the fact that the latter is too deliquescent for commercial purposes.

[1] Birkeland, German Patent, No. 179,882.

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Another modification of this method is due to Schönherr.[1] In his process the arc is stationary and extends over several metres. It is surrounded by a tube through which the air is driven in a spiral current, the spiral being produced by using a rotating jet to introduce the air current into the tube. In this way the mixture of oxygen and nitrogen passes alternately across the arc and into the cooler region on either side, so that it is subjected to a rapid succession of hot and cold periods. This process is said to be the most economical of its kind.

For a discussion of the whole question the reader is referred to Haber's work, *The Thermodynamics of Technical Gas-reactions*. The same author's papers should also be consulted.[2]

3. The Production of Ammonia

In the previous section we dealt with the processes suggested for the union of nitrogen with oxygen, and it was pointed out that the use of oxygen was dictated by its comparative cheapness; in the present section the union of nitrogen with hydrogen will be considered, as, next to oxygen, hydrogen is the least costly element—at least, when it can be utilized in the form of producer gas or some other such mixture.

The work of Regnault[3] on the spark discharge, and that of Donkin[4] upon the silent discharge, had shown that these two forms of electric energy were capable of causing the direct union of nitrogen with hydrogen. It was not till about ten years ago, however, that this process was brought into effective touch with the technical side of the problem.' In 1900, de Hemptinne,[5] using both the types of discharge, made an investigation of the proper conditions under which the action should be carried out. It had been proved by Ramsay and Young[6] that ammonia begins to decompose at a temperature of 500° C., and is completely broken up at a little below 800° C.; so that it was to be expected that the best results would be obtained

[1] *Elektrotechnische Zeitschrift*, 1909, **30**, 865, 897.
[2] Haber and his collaborators, *Zeitsch. Elektrochem.*, 1910, **16**, 11, 789 ff.
[3] Regnault, *Traité de chemie*, 1846.
[4] Donkin, *Proc. Roy. Soc.*, 1878, **21**, 281.
[5] De Hemptinne, *Bull. Acad. roy. Belg.*, **1902**, 28.
[6] Ramsay and Young, *Trans.*, 1884, **45**, 88.

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by synthesis at comparatively low temperatures. This view is confirmed by de Hemptinne's results. He found that the yield was greatest when three conditions were observed: first, the temperature was kept down to the point at which ammonia liquefies; second, the pressure under which the experiment is carried out must be low; and lastly, the gap across which the discharge acts must be narrow. Schlutius[1] has patented a somewhat analogous process in which, instead of a mixture of hydrogen and nitrogen, he employs "Dowson gas," which is obtained by passing a mixture of air and steam over glowing coal. The resulting gas has approximately the following composition :—

	% Volume.
Hydrogen . . .	14
Nitrogen . . .	43
Carbon monoxide . .	39
Carbon dioxide . .	4

This mixture is acted upon by the silent electric discharge in presence of moist platinum, and the nature of the resulting compound depends upon the temperature at which the reaction is carried out. If the apparatus be kept below 80° C., ammonia is formed in accordance with the equation—

$$N_2 + 3H_2 + 2H_2O = 2NH_3,aq.$$

On the other hand, if we allow the temperature to exceed 80° C., the carbon monoxide also reacts, with the formation of ammonium formate—

$$N_2 + 3H_2 + 2CO + 2H_2O = 2H.COONH_4$$

Nithack[2] has applied electrolysis to the ammonia synthesis. His method consists in electrolyzing water which has been saturated with nitrogen under high pressure.

We must now turn to the consideration of the action of catalytic agents upon the union of nitrogen with hydrogen. De Lambilly[3] has investigated this problem, and has taken out a patent for a process based upon his results. He was struck by the fact that the heats of formation of ammonia and ammonium hydrate are less than those of ammonium carbonate

[1] Schlutius, English Patent, No. 2200 (1903).
[2] Nithack, German Patent, No. 95,532.
[3] De Lambilly, German Patent, No. 74;274.

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and ammonium formate. From this it follows that the expenditure of energy required to produce the salts is less than is necessary in the case of the free ammonia or ammonium hydrate. De Lambilly therefore devoted himself to the production of the salts rather than the free substance. His process is as follows. Air and steam are led over white-hot coke, and from the mixture of gases thus produced, either carbon dioxide or carbon monoxide is removed, according as ammonium formate or bicarbonate is required. The gases are then passed through tubes filled with porous substances, such as platinized pumice, wood-charcoal, bone-charcoal, or spongy platinum. After they have passed once through the tubes, the gases are mixed with steam and again sent through the apparatus. The reactions which take place depend upon whether carbon monoxide or carbon dioxide be used—

$$N_2 + 3H_2 + 2CO_2 + 2H_2O = 2HO.CO.ONH_4 . \quad (I.)$$
$$N_2 + 3H_2 + 2CO + 2H_2O = 2H.CO.ONH_4 . \quad (II.)$$

In the case of equation (I.), it is found that the most favourable temperature lies between 40° and 60°, while most ammonium formate is produced between 80° and 130°.

The main fault of the process thus outlined lies in the tendency of the ammonium formate to decompose into water and hydrocyanic acid. In order to evade this difficulty, de Lambilly[1] utilized the same apparatus, but passed through it a mixture of carbon monoxide and ammonia, the latter being obtained from ammonium hydrate. In this case the best temperature seems to lie between 150° C. and 180° C.

It was shown in 1862, by Fleck,[2] that if a mixture of steam, nitrogen, and carbon monoxide were passed over red-hot lime, ammonia was formed. Fleck found that in this reaction, as in the others we have described, the temperature employed was of the greatest importance; in this case it lies somewhere between a dull red and a bright red when the best yields are obtained.

Woltereck[3] passes a mixture of steam and air over iron

[1] De Lambilly, German Patent, No. 78,573.

[2] See Bolley, *Handbuch d. chem. Technol.*, II. 2, 48 (1862).

[3] Woltereck, *Zeitsch. angew. Chem.*, 1904, 17, 1717; *Electrical Review*, 1905, 56, 1721.

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oxide raised to a dull red heat; in technical practice, peat is used to replace the oxide.

Mackey and Hutcheson,[1] in their process, pass heated air in at the bottom of a furnace containing a mixture of coal and carbonate of potash or some other alkali carbonate. By the interaction of these substances a cyanide is produced, which is carried into the upper part of the furnace, where it is broken up by a jet of steam and decomposes into ammonia and a carbonate. The latter falls again into the lower part of the furnace, and the process recommences.

Haber[2] has employed metallic uranium as a catalyst with considerable success.

The last method with which we need deal was originated by Kaiser,[3] and differs from the others in that a stable intermediate compound is formed. Calcium, when heated to redness in a stream of hydrogen, is converted into calcium hydride; and when this body is heated and nitrogen passed over it, calcium nitride is produced. If this in turn be heated in a stream of hydrogen, ammonia is liberated. The process is expressed in the equations below—

$$\text{(I.)} \quad Ca + H_2 = CaH_2$$
$$\text{(II.)} \quad 3CaH_2 + 2N_2 = Ca_3N_2 + 2NH_3$$
$$\text{(III.)} \quad Ca_3N_2 + 6H_2 = 3CaH_2 + 2NH_3$$

It appears to be immaterial whether the gases are allowed to enter the tube together or separately, the action seems to go on with the same ease in either case.

4. The Production of Cyanides

In the foregoing sections we have dealt with the preparation of ammonia and of nitrates, both of which are naturally occurring substances; the present section deals with another set of compounds which at first sight appear most unpromising from the agricultural point of view, owing to their poisonous character. In actual practice, however, the cyanides appear to offer many advantages when used as manures.

[1] Mackey and Hutcheson, English Patent, No. 13,315 (1894).
[2] Haber, *Zeitsch. Elektrochem.*, 1910, **16**, 244.
[3] Kaiser, French Patent, No. 350,966.

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The technical application of cyanides had led to the devising of methods for the production of these substances long before the question of nitrogen fixation became acute. The South African gold industry demanded a heavy output of cyanide for use in the cyanide process of extraction, and consequently a very considerable number of processes have come into existence for the purpose of supplying this need. With these we have no concern here, but will confine ourselves to the chief methods which have been suggested within the last ten years or so.

Next to oxygen and hydrogen, carbon is probably the cheapest element which we can employ to form compounds of nitrogen. Whether it be utilized in the form of coal or coke, it is comparatively cheap and easily procurable, so that it is not surprising that attempts have been made to employ it in the fixation of nitrogen. Before dealing with the later processes which depend directly upon coal, however, we must glance at one or two others which are based upon other substances.

It was long ago shown by Berthelot that if a stream of mixed nitrogen and acetylene was raised to a high temperature, hydrocyanic acid was formed—

$$C_2H_2 + N_2 = 2HCN$$

Hoyermann[1] proposed to utilize this reaction in technical practice by passing a mixture of one part of acetylene and two parts of nitrogen over an electric arc. In this way sixty to seventy per cent. of the acetylene was converted into hydrocyanic acid. The chief drawback of the method lies in the heavy deposits of carbon which take place on the electrodes. O'Neill[2] employed a mixture of air with petroleum vapour or coal-gas, instead of acetylene and nitrogen. Gruszkiewicz[3] utilized "Dowson gas," which he passed over a flaming electrode. The best results were obtained when the percentage of carbon monoxide in the Dowson gas was raised to about fifty.

We must now turn to another set of methods, in which,

[1] Hoyermann, *Chem Zeit.*, 1902, **26**, 70.
[2] O'Neill, *Electrical World*, 1902, **40**, 1009.
[3] Gruszkiewicz, *Zeitsch. Electrochem.*, 1903, 83.

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instead of acetylene, metallic carbides are used. The work of Desfosses,[1] Fownes,[2] Bunsen and Playfair[3] showed that when carbon was heated with non-volatile alkalis, the resulting products contained cyanogen compounds from which ammonia could be obtained. Attempts were thereafter made by various workers to utilize the reaction on a large scale, using barium hydrate as the alkali, but none of them seem to have come to much, owing to the effect which the high temperatures required had upon the apparatus.

The invention of the electric furnace, of course, gave a great impetus to technical research in this department, and as a result most of the difficulties experienced by the older workers have been evaded in modern practice.

The Ampère Electrochemical Company[4] employ the following method. The starting materials are coke and a mixture of barium hydrate and carbonate. The quantities are so chosen as to provide an excess of coke over and above the amount required for the formation of barium carbide; the reason for this is that unless excess of coke is present, the mixture does not possess sufficient porosity to allow the passage of gases through it. The mixture is placed in a revolving electric furnace and the current is switched on. The action which takes place in the heated portion of the furnace is the formation of barium carbide, which fuses and flows over the unaffected part of the coke. The revolution of the furnace now carries this into a colder zone, in which it cools down and solidifies. At this point in the revolution it encounters a stream of nitrogen, which converts the carbide into the cyanide—

$$BaC_2 + N_2 = Ba(CN)_2$$

The further revolution of the furnace brings the formed cyanide into a cooler section, where it is withdrawn from the apparatus. The emptied part of the machine then passes another point, where it is refilled with the mixture of coke and barium salts, and the process continues as before.

[1] Desfosses, *J. Chim. Pharm.*, 1828, **14**, 280.
[2] Fownes, *J. pr. Chem.*, 1842, **26**, 412.
[3] Bunsen and Playfair, *J. pr. Chem.*, 1847, **42**, 397.
[4] *Dingler's Polytech. Jour.*, 1903, **33**, 524.

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In this method[1] there is formed as a bye-product the substance barium cyanamide—

$$BaC_2 + N_2 = BaN \cdot CN + C$$

This substance is a derivative of cyanamide, which in turn is an ammonia substitution product—

$Ba : N \cdot C \equiv N$	$H_2N \cdot C \equiv N$	H_3N
Barium cyanamide	Cyanamide	Ammonia

On repeating the experiment with calcium salts instead of barium ones, it was found that the bye-product of the one reaction became the main product of the second; so that the process yielded chiefly calcium cyanamide. The substance, when heated with water under pressure, liberates ammonia as shown in the following equation :—

$$Ca : N \cdot C \equiv N + 3H_2O = CaCO_3 + 2NH_3$$

The same reaction takes place on long exposure to moist air; so that this substance forms an excellent artificial manure.

5. The Production of Nitrides

In the section on ammonia, we have already mentioned one of the processes by means of which nitrides have been made of service in the nitrogen fixation problem; in the present section we may deal with another method which has been employed. In this department, as in some of the others, the invention of the electric furnace has made practicable in technical work methods which without its aid would never have been of any service on a large scale.

The work of Schützenberger and Colson,[2] following upon that of Deville and Wöhler,[3] showed that two nitrogen compounds of silicon could be obtained, one of which contained carbon in addition to the other two elements. The two substances have the following compositions :—

$$Si_2C_2N \qquad\qquad Si_2N_3$$

[1] Erdmann, *Bericht d. V. Intern. Kongr. f. Angew. Chem.*, 1905, III. 727; Caro, *Zeitsch. angew. Chem.*, 1906, **19**, 1569. See also *Zeitsch. angew. Chem.*, 1903, **16**, 520.

[2] Schützenberger and Colson, *Compt. rend.*, 1882, **94**, 1710.

[3] Deville and Wöhler, *Annalen*, 1859, **110**, 248.

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From the technical point of view it does not much matter which of these substances is formed, or even if a mixture is produced. The nitride, of course, contains a greater percentage of nitrogen than the nitride-carbide, but the difference is not of sufficient importance to make it worth while to take special precautions in order to produce the pure nitride.

Mehner has[1] patented the following process. An oxide of some nitride-forming element, such as silicon, boron, or magnesium, is mixed with coal or coke and submitted to the heat of an electric furnace. Nitrogen is then blown through the mass. As a result, carbon reduces the oxide, yielding the element itself, which is then attacked by the nitrogen to form the nitride—

$$2MgO + C = 2Mg + CO_2$$
$$6Mg + 2N_2 = 2Mg_3N_2$$

When these nitrides are used as artificial manures, any weak acid in the soil, or even carbonic acid, is sufficient to decompose them—

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Their great advantage for agricultural purposes lies in their relatively high percentage of nitrogen, which is nearly double that found in other artificial nitrogenous substances. In this way the cost of carriage is reduced. On the other hand, the cost of manufacture seems at present to be too high to allow them to compete successfully with the products of other processes.

[1] Mehner, German Patent, No. 67,489.

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CHAPTER VIII

SOME HYDROXYLAMINE DERIVATIVES

1. Introductory

If in ammonia the hydrogen atoms be replaced one by one by hydroxyl groups, we shall obtain the following series of substances:—

$$NH_3 \qquad NH_2OH \qquad NH(OH)_2 \qquad N(OH)_3$$

The first two of these are, of course, ammonia and hydroxylamine. The last is the ortho-form of nitrous acid. The remaining body, dihydroxy-ammonia, has recently been prepared by Angeli,[1] who has studied its properties and those of its salts. In the present chapter we shall first give an outline of the methods by which this substance can be prepared, as well as some account of its properties, and shall conclude by a comparison of ammonia with its hydroxy-derivatives. Before dealing with dihydroxy-ammonia (or nitroxyl, to give it a shorter name), we must take up another hydroxylamine derivative, nitro-hydroxylaminic acid, from which nitroxyl can be produced.

2. Nitro-hydroxylaminic Acid

When we take a solution of one gramme molecule of hydroxylamine hydrochloride in alcohol and treat it with an alcoholic solution of two gramme molecules of sodium ethylate, filter off the precipitated sodium chloride, and then add a gramme molecule of nitrobenzene, we obtain a solution from

[1] A complete summary of Angeli's researches is to be found in his pamphlet, *Ueber einige sauerstoffhaltige Verbindungen des Stickstoffs* (1908), which is a translation of his original Italian paper, *Sopra alcuni composti ossigenati dell' azoto* (1907).

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which glittering crystals begin to separate out. If the sodium salt thus obtained is treated with dilute hydrochloric acid at low temperatures, white needle-shaped crystals of melting-point 59° C. are precipitated. On analysis, it is found that these have a composition corresponding to the formula—

$$C_6H_5 . N_2O_2H$$

When we attempt to express the reaction in structural formulæ, the following seems the most probable course:—

$$C_6H_5 . N{:}O + H_2N.OH = C_6H_5 . N{:}N.OH + H_2O$$
$$\quad\quad\quad

From analogy with the case of nitro-benzene, we should deduce that the reaction between ethyl nitrate and hydroxylamine took the course shown in the following equation:—

$$\begin{matrix} C_2H_5O.N{:}O \\ \| \\ O \end{matrix} + H_2N.OH = \begin{matrix} C_2H_5O.N{:}N.OH \\ \| \\ O \end{matrix} + H_2O$$

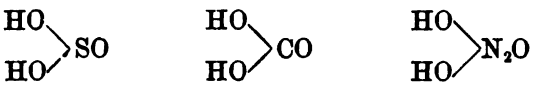
And since the ethyl group and the hydrogen of the hydroxyl group are replaced by sodium atoms in the usual way, we shall obtain in the end—

$$\begin{matrix} NaO.N:N.ONa \\ \| \\ O \end{matrix}$$

We must now turn to examine some of the reactions of this substance. When we treat it with acids, its behaviour offers a strong contrast to that of the corresponding phenyl compound which we have already mentioned. Instead of yielding a stable product, the sodium salt of nitro-hydroxylaminic acid (as this body is termed) gives up nitric oxide violently. Apparently the free acid is unstable and decomposes almost quantitatively according to the equation—

$$H_2N_2O_3 = 2NO + H_2O$$

As Angeli points out, this brings nitro-hydroxylaminic acid into line with sulphurous and carbonic acids, both of which liberate their anhydrides when they are set free from their salts by acids. The parallelism may be brought out by writing the formulæ of the three substances as below—



If, instead of adding acid to a solution of the sodium salt, we allow the latter to stand in the cold, we shall find that nitrous oxide is slowly evolved. If the solution be heated, the decomposition reaction takes place with some violence. The solution, after the nitrous oxide has disappeared, contains nitrite to the extent of half the whole amount of nitrogen in the original salt. The equation for this decomposition can be written thus—

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$$\begin{matrix}NaO.N:NO_2Na\\NaO.N:NO_2Na\end{matrix} + H_2O = N_2O + 2NaNO_2 + 2NaOH$$

Concentrated solutions decompose much more slowly than dilute ones; and the decomposition can be retarded by the presence of soluble sodium salts in the solution.

The sodium salt of nitro-hydroxylaminic acid has a strong reducing action upon silver nitrate. The first stage in the process is the formation of a precipitate of silver nitro-hydroxylaminate—

$$Ag_2N_2O_8$$

which, being very unstable, breaks down almost immediately into silver, nitric oxide, and silver nitrite.

These reactions, however, though interesting in themselves, throw no light upon the constitution of the substances with which we are dealing. More information is to be gained from two other actions in which the sodium salt can be made to take part.

In the first place, when the salt is warmed, it melts to a green liquid which, on analysis, proves to be a mixture of sodium nitrite and hyponitrite. This change we can represent as follows:—

$$\begin{matrix}NaO.N:NO_2Na\\NaO.N:NO_2Na\end{matrix} = \begin{matrix}NaO.N\\\|\\NaO.N\end{matrix} + 2NaNO_2$$

It is evident that the nitrous oxide which is liberated from solutions of the sodium salt of nitro-hydroxylaminic acid is derived from the decomposition of the sodium hyponitrite which is first formed in accordance with the above equation.

Secondly, when we allow the sodium salt of the acid to act upon an aldehyde we obtain the sodium salt of a hydroximic acid. For instance, if we take acetaldehyde we shall produce aceto-hydroximic acid—

$$CH_3.CHO \longrightarrow CH_3.\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}:NOH$$

Now, as can be seen from the formulæ, we have added to the group —CHO the group NOH. Further, it is found

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that in this case also sodium nitrite is present in the solution at the end of the reaction: and from an estimation of the quantities of the two end-products obtained, it is found that the reaction takes the following course and gives a quantitative yield :—

$$H_2N_2O_3 = HNO_2 + HNO$$

These reactions cannot be explained with any probability except by the assumption that the sodium salt of nitro-hydroxylaminic acid has the constitution which we assigned to it, viz.—

$$\begin{matrix} N\,.\,ONa \\ \| \\ NO_2\,.\,Na \end{matrix}$$

Before leaving this part of the subject, we might deal with one point which is of some theoretical interest. We have mentioned that the action of nitro-hydroxylaminic acid (in the form of its sodium salt) upon aldehydes is to give hydroximic acids according to equation (I.). Now, on boiling with dilute acids, these hydroximic acids are broken down into hydroxylamine and an organic acid in the way shown in equation (II.).

$$\text{(I.)}\quad \begin{matrix} NOH \\ \| \\ NO_2H \end{matrix} + R\,.\,CHO = \begin{matrix} NOH \\ \| \\ R\,.\,C\,.\,OH \end{matrix} + NO_2H$$

$$\text{(II.)}\quad \begin{matrix} NOH \\ \| \\ R\,.\,C\,.\,OH \end{matrix} + H_2O = \begin{matrix} O \\ \| \\ R\,.\,C\,.\,OH \end{matrix} + NH_2OH$$

When nitro-hydroxylaminic acid is treated with dilute acids, it ought thus by analogy to decompose into nitric acid and hydroxylamine, the equation for which reaction would be parallel to (II.)—

$$\begin{matrix} NOH \\ \| \\ O:N.OH \end{matrix} + H_2O = \begin{matrix} O \\ \| \\ O:N.OH \end{matrix} + NH_2OH$$

No such reaction takes place, however, for the product would be nitrate of hydroxylamine, which is a perfectly stable body and easy to detect. As we have seen above, what actually

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occurs when the sodium salt is treated with acids is a violent decomposition of the salt with the evolution of nitric oxide—

$$H_2N_2O_3 = 2NO + H_2O$$

Something evidently takes place in the series of reactions shown in (I.) and (II.) which does not occur in the direct action of acids upon the salt. If we add together the two equations (I.) and (II.), and then write the group R.CO.OH as R.CO.H + O, we shall get the following result after cancelling out the substances common to both sides:—

$$\begin{matrix} NOH \\ \| \\ NO_2H \end{matrix} + H_2O = \begin{matrix} NH_2OH \\ \\ NO_2H \end{matrix} + O$$

In other words, in the course of the reactions (I.) and (II.), we have brought about a new species of decomposition of nitrohydroxylaminic acid, the products being nitrous acid, hydroxylamine, and oxygen.

Thus in the foregoing paragraphs we have described no less than six different ways in which this acid can be decomposed. We may tabulate them here for the sake of clearness, adding in each case the material which forms the starting-point of the reaction—

Free acid . . .	$H_2N_2O_3 = 2NO + H_2O$
Silver salt . . .	$H_2N_2O_3 = HNO_2 + NO + H$
Sodium salt . . .	$H_2N_2O_3 = HNO_2 + HNO$
„ „ . . .	$2H_2N_2O_3 = 2HNO_2 + (NOH)_2$
„ „ . . .	$2H_2N_2O_3 = 2HNO_2 + N_2O + H_2O$

and finally the indirect decomposition through the hydroximic acids—

$$H_2N_2O_3 + H_2O = HNO_2 + O + NH_2OH$$

3. Nitroxyl

The substance nitroxyl or dihydroxy-ammonia has not yet been isolated in the free state, owing to its extreme instability; but its properties have been studied by means of its solutions. In the previous section we discussed one reaction during which nitroxyl appears to be formed as an intermediate product; and

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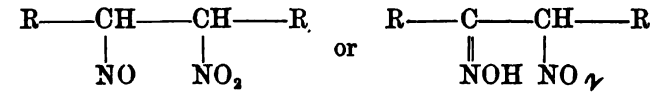
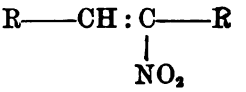
we must now deal with one or two other methods by means of which we can obtain this body.

Many unsaturated carbon compounds when treated with nitrous acid take up N_2O_3, and are converted into nitrosites of the formula—



Angeli chose the nitrosite of iso-safrol as the starting-point of his work. When this nitrosite is treated with alkalis, it yields an unsaturated nitro-derivative, which we can represent by the formula—



The equation for the reaction may be written in full as follows:—

$$[(CH_2O_2).C_6H_3.C_3H_5.N_2O_3]_2 = 2(CH_2O_2).C_6H_3.CH:C(NO_2).CH_3 + 2NOH$$

Nitrosite of iso-safrol. Nitro-compound.

Angeli proved the presence of hyponitrous acid in the solution by means of the characteristic silver salt; and as he found that the solution converted aldehydes into hydroximic acids, the presence of nitroxyl was also demonstrated.

Divers and Haga[1] showed that when hydroxylamine sulphonic acid was hydrolyzed by means of caustic potash, the end-products of the reaction were the potassium salts of sulphurous and hyponitrous acids. They therefore formulated the reaction in the following manner:—

$$2HO.NH.SO_3K + 4KOH = 2K_2SO_3 + 2HO.NH.OK + 2H_2O$$
$$2HO.NH.OK = 2H_2O + KON:NOK$$

Angeli found that when treated with aldehydes in presence of alkali, this sulphonic acid yields hydroximic acids and sulphites; and from this he concludes that the structure of the sulphonic acid could be better expressed as analogous to that of nitrohydroxylaminic acid, thus—

$$HO.N:SO(OH)_2$$

[1] Divers and Haga, *Trans.*, 1889, **55**, 760.

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The decomposition in presence of alkali would then be expressed by the simple equation—

$$HO.N:SO(OK)_2 = NOH + SO(OK)_2$$

Again, take the case of benzene sulphohydroximic acid. This body was discovered by Piloty,[1] who ascribed to it the constitution—

$$C_6H_5 . SO_2 . NH . OH$$

By the action of alkali, it yields a hyponitrite as well as the salt of benzene sulphinic acid—

$$2C_6H_5 . SO_2 . NH . OH + 4KOH = 2C_6H_5 . SO_2 . K + (NOK)_2 + 4H_2O$$

Since in this case also aldehydes react with the body in presence of alkali, Angeli deduces that here too nitroxyl must be formed as an intermediate product; and the decomposition in presence of alkali must follow the course shown in the equation—

$$HO . N : SO(OH) . C_6H_5 = HON + C_6H_5 . SO_2 . H$$

The parallelism in behaviour in the three substances, nitrohydroxylaminic acid, hydroxylamine sulphonic acid, and benzene sulpho-hydroximic acid, is thus expressed by the three perfectly analogous formulæ—

NOH	NOH	NOH
‖	‖	‖
NO . OH	HO . SO . OH	C_6H_5 . SO . OH

It will be remembered that hydroxylamine itself can act either as an oxidizing or as a reducing agent. Haber[2] has shown that hydroxylamine hydrochloride reduces ferric chloride to ferrous chloride; while in alkaline solution ferrous hydroxide is converted into ferric hydroxide in presence of hydroxylamine. This alteration of properties might be explicable by assuming that in presence of alkali hydroxylamine becomes converted into an unstable dibasic hydroxide—

$$H_3N(OH)_2$$

Now, when we come to the hydroxylamine derivatives of acids, we find that they in turn behave differently according to

[1] Piloty, *Ber.*, 1896, **29**, 1560. [2] Haber, *Ber.*, 1896, **29**, 2444.

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whether they are hydrolyzed by acids or alkalis. With alkalis the sulphonyl derivatives * give sulphinic acids, while with acids the hydrolysis yields sulphonic—

$$\text{Alkaline hydrolysis } \begin{matrix}\text{R . SO}_2\text{ . NH(OH)}\\ \text{H . OH}\end{matrix} \rightarrow \text{R . SO}_2\text{ . H} + \text{NH(OH)}_2$$

$$\text{Acid hydrolysis } \begin{matrix}\text{R . SO}_2\text{ . NH(OH)}\\ \text{HO . H}\end{matrix} \rightarrow \text{R . SO}_3\text{ . H} + \text{NH}_2\text{ . OH}$$

Thus in the acid hydrolysis, we find that the group R . SO_2— is replaced by a hydrogen atom; while in the alkaline hydrolysis it is exchanged for a hydroxyl radicle.

We must now deal with a few of the characteristic reactions of nitroxyl. There is, in the first place, the reaction with aldehydes which we have had occasion to mention several times. This reaction can be employed as a method of distinguishing aldehydes from ketones, though in certain cases it fails to take place: it is also a useful means of separating ketones from aldehydes in a mixture.

If we allow a solution of nitroxyl, obtained from the salt of nitro-hydroxylaminic acid, to react with an alkyl iodide, the end-product of the reaction is an oxime—

$$\text{R.CH}_2\text{.I} + \text{H.NO} = \text{R . CH}_2\text{.NO} + \text{HI}$$
$$\text{R . CH}_2\text{.NO} = \text{R.CH:NOH}$$

and since, of course, we can obtain hydroxylamine from an oxime by hydrolysis with acids—

$$\text{R . CH : NOH} + \text{H}_2\text{O} = \text{R . CHO} + \text{NH}_2\text{OH}$$

this reaction practically corresponds to a reduction of dihydroxy-ammonia to hydroxylamine; while at the same time the alkyl iodide is converted into an aldehyde. Since the alkyl iodide belongs to the same series as the alcohols, we have thus carried out a simultaneous oxidation and reduction process in which the oxidizing agent has been dihydroxy-ammonia. A converse process has been known for a considerable time. If we treat an aldehyde with hydroxylamine, we obtain an oxime, which on loss of water is converted into a nitrile; this in turn can be hydrolyzed by acids, giving ammonia. We have thus

* Nitro-hydroxylaminic acid is an exception.

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reduced hydroxylamine to ammonia, and oxidized the aldehyde to an acid. The steps are shown in the equations below—

$$R.CHO + NH_2OH = R.CH:NOH + H_2O$$
$$R.CH:NOH = R.CN + H_2O$$
$$R.CN + 2H_2O = R.COOH + NH_3$$

When nitroxyl is allowed to act upon nitroso-derivatives, it forms nitroso-hydroxylamine derivatives. With nitroso-benzene we thus obtain the same substance as we produced by the action of hydroxylamine upon nitro-benzene; and in this way the formula which we originally ascribed to it is placed beyond doubt—

$$C_6H_5.\overset{\overset{\cdot\cdot}{O}}{\underset{\|}{N}} + \ddot{N}OH = C_6H_5.\underset{\|}{N}:NOH$$
$$\qquad\qquad\quad O \qquad\qquad\qquad\quad O$$

The action of nitroxyl upon secondary amines gives rise to tetrazones, that is, compounds in which there is a chain of four nitrogen atoms directly attached to each other. The action can be best explained by assuming that its first stage is the formation of an intermediate product—

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!NH + NH(OH)_2 = \begin{matrix} R \\ R \end{matrix}\!\!>\!N.NH.OH + H_2O$$

Two of the intermediate compound molecules then lose water and unite to yield the tetrazone—

$$\begin{matrix} R_2:N.NH.OH \\ R_2:N.NH.OH \end{matrix} = 2H_2O + \begin{matrix} R_2:N.N \\ \quad\| \\ R_2:N.N \end{matrix}$$

When we use a substituted hydroxylamine instead of a secondary amine, the reaction takes a course almost parallel to that outlined above; in this case also a molecule of water splits out, yielding a diazo-hydroxide—

$$\begin{matrix} R \\ HO \end{matrix}\!\!>\!NH + NH(OH)_2 = \begin{matrix} R \\ HO \end{matrix}\!\!>\!N.NH.OH + H_2O$$

$$\begin{matrix} R \\ HO \end{matrix}\!\!>\!N.NH.OH = \begin{matrix} R \\ HO \end{matrix}\!\!>\!N{\equiv}N + H_2O$$

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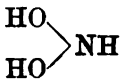
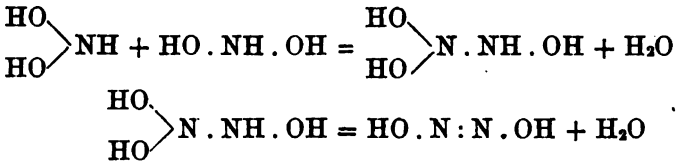
These last two reactions now allow us to approach the question of the formation of hyponitrites which we have touched upon several times in the course of this chapter. If we write down the formula for dihydroxy-ammonia—

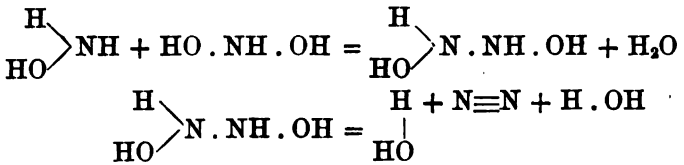


its resemblance to that of a secondary amine is evident; we have simply two hydroxyl groups instead of alkyl radicles. Now let us imagine that dihydroxy-ammonia could behave towards itself just as it does towards a secondary amine. The interaction of the two molecules would then be represented in the following way :—



In this manner the mechanism of the production of hyponitrites from dihydroxy-ammonia becomes quite comprehensible.

Finally, we may deal with the action of nitroxyl upon hydroxylamine and hydrazine. In the case of hydroxylamine itself, the reaction probably runs parallel to that which we have already described in the case of the substituted hydroxylamines. The evolution of nitrogen which takes place would thus be explained by the following changes :—



When hydrazine is substituted for hydroxylamine, the reaction products are nitrogen, ammonia, and water. This could be explained on the scheme shown below—

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$$\begin{matrix}NH_2\\H\end{matrix}\!\!>\!NH + HO.NH.OH = \begin{matrix}NH_2\\H\end{matrix}\!\!>\!N.NH.OH + H_2O$$

$$\begin{matrix}NH_2\\H\end{matrix}\!\!>\!N.NH.OH = \begin{matrix}NH_2\\|\\H\end{matrix} + N{\equiv}N + H.OH$$

We have now given an account of the properties of nitroxyl, and can devote our attention to the question of its probable structure. From the reactions with which we have dealt, it seems probable that the substance has the constitution shown by one of the two possible desmotropic forms—

$$N{\equiv}O{-}H \qquad H{-}N{=}O$$

Angeli has, however, adduced evidence to show that it is more likely that nitroxyl in solution exists as the hydrate of NOH—in other words, as dihydroxy-ammonia.

Bamberger and Tschirner[1] have proved that when primary amines are oxidized with Caro's reagent they are converted into substituted hydroxylamines—

$$R.NH_2 \rightarrow R.NH.OH$$

Angeli found that when hydroxylamine was submitted to the same oxidation process, the solution thus obtained gave the nitroxyl reaction with aldehydes. In this case no hydroxylamine could have remained unchanged, for the solution did not reduce Fehling's solution, though it did reduce ammoniacal silver nitrate. It appears probable, therefore, that the oxidation of hydroxylamine with Caro's reagent takes the following course:—

$$HO.NH_2 \rightarrow HO.NH.OH$$

The action of nitroxyl upon aldehydes would then take place in the following stages:—

$$R.CHO + HN(OH)_2 = R.CH\begin{matrix}N(OH)_2\\OH\end{matrix} = H_2O + R.C\begin{matrix}NOH\\OH\end{matrix}$$

4. Ammonia and its Hydroxyl Substitution Products

We are now in a position to examine the series of substances which are produced when one or more of the hydrogen atoms

[1] Bamberger and Tschirner, *Ber.*, 1899, **32**, 1676.

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in ammonia are replaced by hydroxyl radicles. We should thus obtain the following series of compounds:—

NH_3	.	Ammonia
NH_2OH	.	Hydroxylamine
$NH(OH)^2$	.	Dihydroxy-ammonia or nitroxyl hydrate
$N(OH)_3$	.	Ortho-form of nitrous acid

The first member of the series is a weak base; hydroxylamine is a still weaker base; nitrous acid is a weak acid; it seems therefore probable that dihydroxy-ammonia is a neutral substance.

The relative stabilities of the four compounds diminish as we accumulate hydroxyl groups in the molecule: ammonia is a perfectly stable substance; hydroxylamine is unstable in the free condition; dihydroxy-ammonia is not yet isolated; and, of course, the ortho-form of nitrous acid does not exist except perhaps in solution. On the other hand, the introduction of hydroxyl groups increases the acidic character of the bodies.

When we examine the action of the four substances upon aldehydes, the differences between them stand out very clearly. The reactions are expressed in the following equations:—

$$R.CHO + NH_3 = R.CH(OH).NH_2$$
$$R.CHO + NH_2OH = R.CH:NOH + H_2O$$
$$R.CHO + NH(OH)^2 = R.C(OH):NOH + H_2O$$

Nitrous acid is without action upon aldehydes. Upon ketones, the positions are reversed to some extent: nitrous acid reacts with the neighbouring methylene group if there be one; dihydroxy-ammonia does not react at all; hydroxylamine produces oximes; while ammonia does not add itself on to the carbonyl group.

We may mention just one more series of reactions. It is well known that in the diazo-reaction nitrous acid acts upon a primary amine, and that from the solution we can liberate all the nitrogen originally present in the amine and the nitrous acid. The equation is as follows:—

$$R.NH_2 + ON.OH = R.N:N.OH + H_2O = R.OH + N_2 + H_2O$$

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If this could be applied to the parent substance, the equation would take the following form :—

$$NH_3 + N(OH)_3 = N_2 + 3H_2O$$

A precisely similar reaction takes place between hydroxylamine and dihydroxy-ammonia in aqueous solution at ordinary temperatures—

$$NH_2OH + NH(OH)_2 = N_2 + 3H_2O$$

This reaction occurs only when there is a good excess of hydroxylamine present; if this is not the case, then the dihydroxy-ammonia is apt to condense with a second molecule of itself to produce hyponitrous acid.

A parallel set of reactions in which nitrous oxide is evolved instead of nitrogen has also been discovered—

$$NH_3 + ON(OH)_3 = N_2O + 3H_2O$$
$$NH_2OH + N(OH)_3 = N_2O + 3H_2O$$
$$NH(OH)_2 + NH(OH)_2 = N_2O + 3H_2O$$

From these instances it is easy to deduce the influence exerted on the properties of the substances by the successive replacement of the hydrogen atoms by hydroxyl radicles.

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CHAPTER IX

THE COBALTAMMINES

1. General

In the eighth column of the Periodic Table we find a group of three elements, iron, nickel, and cobalt, which, while resembling each other in a general way, show the usual slight differences in their chemical properties. All three form chlorides in which one atom of the metal is combined with two atoms of chlorine;

$$FeCl_2 \qquad NiCl_2 \qquad CoCl_2$$

but when an attempt is made to produce a higher chloride, it is found that while the ferric chloride, $FeCl_3$, is quite stable, the corresponding cobalt compound $CoCl_3$, exists only in solution, and no analogous nickel salt can be produced at all. From this it appears probable that the highest valency which we can reasonably ascribe to cobalt is three.

If to a solution of cobaltous chloride, we add ammonia until the first-formed precipitate dissolves, allow the solution to stand in air until the original brown colour is changed to red, and then add concentrated hydrochloric acid, we obtain a precipitate of bright scarlet crystals. This new substance, which is called roseo-cobalt chloride, is found on analysis to have an empirical formula corresponding to the composition—

$$CoCl_3 + 5NH_3 + H_2O$$

Again, if we precipitate and redissolve the cobaltous hydroxide in excess of ammonia as before, but this time add to the solution a large quantity of ammonium chloride, we shall find that after standing in the air and treatment with hydrochloric acid it gives a yellow-brown precipitate, luteo-cobalt chloride, whose empirical formula may be written thus—

$$CoCl_3 + 6NH_3$$

These compounds are typical examples of the class of cobalt

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ammonia derivatives with which we shall deal in the present chapter. It is found that they may be conveniently divided into classes according to the number of ammonia molecules which they contain; and in this way we obtain the following groups:—

Name.	Formula.
Hexammine series . . .	$CoX_3 + 6NH_3$
Pentammine series . . .	$CoX_3 + 5NH_3$
Tetrammine series . . .	$CoX_3 + 4NH_3$
Triammine series . . .	$CoX_3 + 3NH_3$
Diammine series . . .	$CoX_3 + 2NH_3 + MX$

Here X represents an electro-negative atom or group, and M an electro-positive one.

Now, research has shown that these ammonia groups are not attached in a loose way, but are actually in some manner bound up with the original cobalt salt. Further, they are so closely attached as to produce a complete change in the chemical character of the compound; for while in the salt CoX_3 we can detect the presence of the atoms X by the usual analytical methods, in the case of many cobaltammines the X atoms appear to lose their ordinary chemical character. The problem before chemists, therefore, is twofold. In the first place, we have to find some explanation of the addition of several ammonia groups to a compound such as cobaltic chloride, in which, as we have seen, the affinity of the cobalt atom already appears to be completely saturated by that of the three chlorine atoms. Secondly, we must show why this addition of ammonia molecules has such a far-reaching effect upon the chemical behaviour of the chlorine atoms.

Since the problem of the cobaltammine constitution is a special case of the general question of the constitution of complex salts, it is hardly to be wondered at that the suggestions proposed at various times are now fairly numerous. The chief of these hypotheses we shall deal with in the succeeding sections of this chapter.

2. Theories of the Cobaltammines

(a) *The Blomstrand-Jörgensen Theory*

It is not necessary in this place to enter into any detailed account of the historical development of the metal-ammonia

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question. Reitzenstein[1] has traced its evolution, and reference may be made to his paper for further information. The first important step was taken by Berzelius in the consideration of the ammonia compounds of platinum salts, which in some respects resemble the cobaltammines. On the dualistic hypothesis of Berzelius, metal-ammonia compounds were produced by the union of ammonia with another complex; this complex was not split off by treatment with acids, and did not affect the "saturation-capacity" of the base. To express this idea, Berzelius used formulæ of the following type:—

$$Pt.\overline{NH_2}.\overline{NH_4}\,\overline{Cl}$$

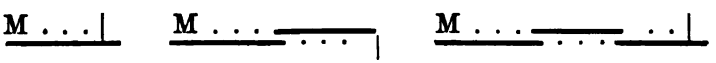
In the succeeding quarter of a century the ideas of Berzelius receded into the background, and it was not until 1869 that they were recalled by Blomstrand in his *Chemie der Jetztzeit*.[2] Blomstrand,[3] while taking Berzelius' formula, preferred to modify it in order to make it represent a true ammonia derivative, and in this way he arrived at the following symbol:—

$$Pt.\overline{NH_3}.\overline{NH_3}.\overline{Cl}$$

which, when reduced to the modern system of nomenclature, becomes—

$$\begin{matrix} NH_3.NH_3.Cl \\ Pt \\ NH_3.NH_3.Cl \end{matrix}$$

A somewhat similar view had been taken by Odling. This formula carries the implicit assumption that the group —NH_2—, like —CH_2—, has the faculty of forming homologous chains. Blomstrand recognized this, and represented the metal-ammonia derivatives by means of symbols of the following types:—



If we assume the possibility of such a linkage of nitrogen atoms, we must take into account, as Blomstrand himself pointed out, the possibility of two forms of chain formation; for just as in the carbon compounds we may have the normal

[1] Reitzenstein, *Zeitsch. anorg. Chem.*, 1898, **18**, 152.
[2] See also Wurtz, *Dictionnaire de Chimie*, i. 947 (1869).
[3] Blomstrand, *Ber.*, 1871, **4**, 40.

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form (I.) and the iso-form (II.), so in the nitrogen chains we may have the normal form (III.) and the iso-form (IV.)—

(I.) $R—CH_2—CH_2—R$ (II.) $R—\overset{\displaystyle CH_3}{\overset{|}{CH}}—R$

(III.) $R—NH_2—NH_2—R$ (IV.) $R—\overset{\displaystyle NH_4}{\overset{|}{NH_2}}—R$

Blomstrand pointed out that a structure of the type (IV.) was not at all probable, owing to the fact that while the four valencies of carbon are apparently equivalent, the fifth valency of the nitrogen atom is always attached to a negative radicle; so that the radicle NH_4 could hardly be expected to unite with another nitrogen atom. At that time, however, the subject was not sufficiently studied to make a decision on the point possible; and it was not until Jörgensen began his series of researches on the metal-ammonia compounds that the question was settled.

In the early days of research upon the metal-ammonia compounds, it was supposed that the cobalt-ammonia molecule contained two cobalt atoms, so that the formula of the pentammine salts, for example, was written thus—

$$Co_2Cl_6,10NH_3$$

Jörgensen[1] from molecular weight determinations, showed that the molecule contained only one cobalt atom, so that the true molecular formula is—

$$CoCl_3,5NH_3$$

In order to avoid confusion, we may transliterate the statements made in his earlier papers into the true formulæ.

In 1879, Jörgensen[2] took up the question of the chloro- and bromo-pentammine salts, which have the empirical formulæ—

$$CoCl_3,5NH_3 \qquad CoBr_3,5NH_3$$

and he found that in both series of salts one of the halogen atoms was connected more closely than the others with the rest of the molecule. This conclusion he based upon the following evidence. (1) In double decompositions carried out in the cold, one halogen atom remains associated with the

[1] Jörgensen, *J. pr. Chem.*, [2] 1890, **41**, 440. [2] *Ibid.*, [2] 1879, **19**, 49.

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cobalt and ammonia instead of being split off like the other two—for instance, it is not removed by silver nitrate; (2) though concentrated sulphuric acid breaks off two halogen atoms in the form of haloid acid, it leaves the third halogen atom unattacked; (3) in the formation of double salts, two halogen atoms are alone concerned; (4) if for a chlorine atom in the chloro-pentammine salt we substitute a bromine atom, we can produce two different salts which differ in molecular volume from each other, as the following figures show :—

Substance.	Molecular volume.	
$Br(Co,5NH_3)Cl_2$	281·6	
$Cl(Co,5NH_3)Cl_2$	277·7	
		Diff. = 3·9
$Cl(Co,5NH_3)Br_2$	319·9	
$Cl(Co,5NH_3)Cl_2$	277·7	
		Diff. = 42·2

Thus in the first case the replacement of chlorine by bromine produces a difference of 3·9 in molecular volume, while in the case where the other type of chlorine atom is similarly replaced the difference in molecular volume is $42{\cdot}2 \div 2$. In order to express these differences between the two sets of halogen atoms, we might write the formulæ of the salts as shown in the foregoing table; but since the third halogen atom appears to be associated in some way with the cobalt and ammonia, we might express the character of the compounds better by the following formulæ :—

$$[Co,Cl,5NH_3]Cl_2 \quad [Co,Br,5NH_3]Cl_2 \quad [Co,Cl,5NH_3]Br_2$$

We must now concern ourselves with the constitution of the groups enclosed within the square bracket. It will be remembered that the question at issue was whether (supposing the ammonia groups to be united in a chain) the chain was a normal one or a forked one. Let us consider the latter case. Since the metal-ammonia compounds are formed from a metallic salt and ammonia, it is obvious that one ammonia must lose a hydrogen atom, while another ammonia is changed to ammonium by the gain of that hydrogen. The formulæ below show the only possible mechanism for the reaction—

$$\text{(I.)} \qquad M{-}X + NH_3 = M{-}NH_3{-}X$$

$$\text{(II.)} \quad M{-}NH_3{-}X + NH_3 = M{-}\underset{\displaystyle NH_4}{\underset{|}{NH_2}}{-}X$$

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Thus far the formation of the forked chain, the presence of the labile hydrogen in the ammonia group is a *sine quâ non.*

Jörgensen[1] attacked the problem in an ingenious way. If the labile hydrogen atom was essential to the production of the forked chain, then no forked chain could be produced by the interaction of a tertiary amine with a metallic salt; and to make doubly sure, Jörgensen chose as his amine pyridine, in which there is no possibility of decomposition. Had he used trimethylamine, for example, it might have been suggested that one of the methyl groups was labile, but this argument could not possibly be advanced in the case of pyridine. When the metallic salt was allowed to interact with pyridine, it was found that metal-pyridine compounds were formed which were in every way analogous to the metal-ammonias. By this means it was shown that the latter class of substances did not contain the group $—NH_4$.

We now come to a point where our ordinary ideas of metallic salts cannot help us much. As was mentioned above, Jörgensen has shown that the pentammine salts have two halogen atoms which take part in the ordinary reactions, while a third halogen atom apparently is not ionized, but acts as if it were attached to the rest of the molecule in the same way as bromine is attached in bromo-benzene. To express this Jörgensen adopted the Blomstrand formula, assumed the division of the ammonia groups into chains (one being a main chain of four ammonia groups), and postulated that halogen atoms or electro-negative radicles directly attached to the cobalt atom were not ionized in solution. By this means he arrived at formulæ of the following type:—

$$\begin{array}{l} \quad Cl^{*} \\ \quad\diagup \\ Co—NH_3—Cl \\ \quad\diagdown \\ \quad NH_3.NH_3.NH_3.NH_3.Cl \end{array}$$

Here the chlorine atom marked with an asterisk is the one which is not ionized; the other two have the same properties as the chlorine in ammonium chloride.

On first coming into contact with these formulæ, the

[1] Jörgensen, *J. pr. Chem.*, [2] 1886, **33**, 489.

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ordinary chemist feels, for some reason or other, that "something is wrong." On a closer inspection, however, it will be found that there is nothing in them which differs in kind from what we meet every day; it is merely the way in which the formulæ are written that at first sight makes them seem strange. For instance, we usually write the hydrochloride of hydrazine as in (I.); if we write it as in (II.), the analogy with the Jörgensen cobaltammine formulæ is better brought out—

(I.) $HCl.NH_2—NH_2.HCl$ (II.) $Cl—NH_3.NH_3.Cl$

In the case of the hydroxylamine salts, it seems probable that similar chains are formed. For instance, dihydroxylamine hydrochloride[1] might be written in the following way—

$$H—NH_2(OH)—NH_2(OH)—Cl$$

while trihydroxylamine hydriodide[2] may be be supposed to have the constitution—

$$H-NH_2(OH)-NH_2(OH)-NH_2(OH)-I$$

So far, we have dealt only with those compounds which are made up of a metallic salt and ammonia, but we must now consider a second type of the cobalt-ammonia class. In these new substances, it is found that one or more of the ammonia molecules can be replaced by a corresponding number of water-molecules. To express this, Jörgensen[3] formulated these bodies as oxonium derivatives, thus—

$$\begin{matrix} & Cl & & & & \\ & / & & & & \\ Co & —Cl & & & H & \\ & \backslash & & & | & \\ & NH_3.NH_3.NH_3. & & & O & .Cl \\ & & & & | & \\ & & & & H & \end{matrix}$$

This, then, is the Jörgensen-Blomstrand theory. Although

[1] Lossen, *Annalen*, 1871, **160**, 242.

[2] Dunstan and Goulding, *Trans.*, 1896, **69**, 838; see also Piloty and Ruff, *Ber.*, 1897, **30**, 1656.

[3] Jörgensen, *Zeitsch. anorg. Chem.*, 1897, **11**, 448; **14**, 417–8; 1899, **19**, 109.

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at first sight it may appear to contain some rather unusual features, it must be borne in mind that in the metal-ammonias we have a series of substances without parallel among our simple salts. If we recognize this, we shall not run the risk of rejecting, through prejudice, either the idea of ammonia chains or the hypothesis that a halogen atom directly connected with a metal may not ionize in solution.*

(*b*) *The Werner Hypothesis*

In 1893 Werner[1] put forward an hypothesis, by the aid of which he hoped to give a complete explanation, not only of the properties of metal-ammonia compounds, but of hydrates as well. We must take up in turn the series of assumptions upon which his views are based.

I. He assumes the existence of two different forces which go to link together the atoms of a molecule. In the first place, there are what he calls "*main valencies*," which correspond to "our ordinary valencies"; and, secondly, there are so-called "*auxiliary valencies*," "which must be assumed to explain the constitution of molecular compounds." To make clear the difference between the two he gives the following definitions[2]: (*a*) "Main valencies unite together simple or compound radicles which can exist as independent ions or whose chemical binding-power is equivalent to that of the ionizable radicles. (*b*) Auxiliary valencies represent actions of affinity which unite together radicles that neither act as independent ions nor can be equivalent thereto." He further defines the two terms thus: (1) "Main valencies are those whose saturation-power is measured by equivalence with one electron. (2) By an auxiliary valency is understood an action of affinity which can unite two atomic groups by '*atomare*' union, but is not capable of chaining up an electron." Finally,[3] to make the matter quite clear, he adds, "Main and auxiliary valencies are actions of affinity which

* Compare the cases of mercuric chloride and cyanide.

[1] Werner, *Zeitsch. anorg. Chem.*, 1893, **3**, 267. See also his *Lehrbuch der Stereochemie*, 1904. Full references to the literature of the metal-ammonias are given by him in *Ber.*, 1907, **40**, 15.

[2] Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, pp. 58–9. 1905.

[3] Werner, *Lehrbuch der Stereochemie*, p. 318. 1904.

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apparently differ only in their order of magnitude, as a metre from a part thereof."

II. His second assumption (the evidence for which we shall examine in a later section) is as follows: If we take the compounds shown below—

(I.)	(II.)	(III.)	(IV.)
$CoX_3,3NH_3$	$CoX_3,4NH_3$	$CoX_3,5NH_3$	$CoX_3,6NH_3$

Werner lays it down that when (I.) is dissolved in water no ions are formed, the substance not being dissociated. In the case of (II.), one of the "X" groups is supposed to ionize; in (III.) two "X" ions are formed; while in (IV.) there are three. That is to say, if Werner be correct, we must write the formulæ of the four bodies thus, in order to bring out their behaviour in solution—

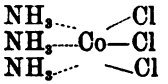
(I.)	(II.)	(III.)	(IV.)
$(CoX_3,3NH_3)$	$(CoX_2,4NH_3)X$	$(CoX,5NH_3)X_2$	$(Co,6NH_3)X_3$

Thus, in order to go from the compound (IV.) to (III.) one of the acid radicles "X" loses its acid character, ceases to act as an ion, and replaces one of the ammonia radicles within the bracket.[1] In the compound (I.) this process has reached its limit, three acid groups being within the bracket, and hence forming part of the complex radicle.

III. Werner's next assumption is identical with that of Jörgensen, viz. that acid radicles directly attached to the cobalt atom are not ionized when the substance is dissolved in water.

IV. He further assumes that all the groups within the brackets are directly attached to the cobalt atom, whether they be halogen atoms, nitro-groups, or ammonia molecules.

V. He assumes, in the fifth place, that the groups within the brackets are united to the cobalt atom by means of his postulated "auxiliary valencies." It does not seem quite clear whether he means that the chlorine atoms in such a compound as—



are united to cobalt by a so-called "auxiliary" valency or

[1] Compare, however, Jörgensen's remarks, *Zeitsch. anorg. Chem.*, 1894, 7, 317–320.

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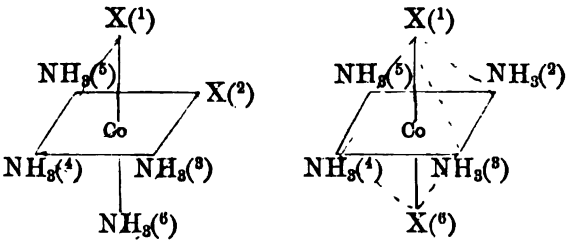
not. According to his definition they must be; but in cases where he distinguishes between "main" and "auxiliary" valencies, he uses the ordinary straight line to represent an ordinary valency, and a dotted line to represent an "auxiliary" one; it therefore seems peculiar to find in some of his formulæ a mixture of the two symbols, such as is shown above.

VI. He next assumes that each of the six groups within the bracket is placed at the corner of a regular octahedron, whose centre is occupied by the cobalt atom.

VII. In the seventh place he makes the further implicit assumption that, except when intramolecular wandering of groups is required to make the hypothesis fit the facts, the six groups retain in space their relative positions with regard to each other and to the cobalt atom. On this assumption, it is evident that a compound of the type—

$$\left[\begin{matrix} & (NH_3)_4 & \\ Co & & \\ & X_2 & \end{matrix}\right] X$$

could exist in two isomeric forms, according to whether the two "X" groups lay at opposite ends of the same edge of the octahedron or not. The two possible formulæ are shown in the figures below, which also give the system of numbering proposed by Werner for the corners of his octahedron—



These seven assumptions, together with some others which we need not detail, make up what Werner calls his "Co-ordination theory," the gist of which is that the six groups within the brackets are directly attached to (or, as he calls it, "co-ordinated with") the cobalt atom, by means of some sort of force which is the same kind of thing as an ordinary valency, without exactly being one. He has applied the same ideas to

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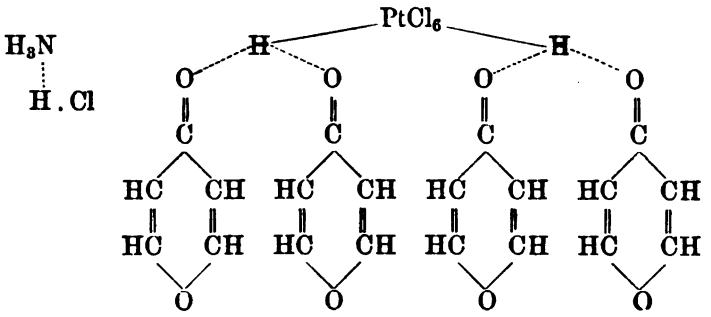
the case of ammonium salts[1] and oxonium salts,[2] producing formulæ like—



In these cases the hydrogen atoms are assumed to be more than monovalent, and the ammonia radicle or pyrone group is attached to the hydrogen atom by means of a so-called "auxiliary valency."

With regard to Werner's first assumption, that of the so-called "main" and "auxiliary" valencies, Jörgensen[3] has pointed out that it leads to confusion when applied to the rest of Werner's ideas about the cobaltammines. "If one atom of chlorine or another electro-negative radicle is supposed, for instance, to be co-ordinated with the trivalent cobalt atom, and does not saturate a valency of that atom, it is incomprehensible why the radicle thus formed, $Co(NH_3)_5Cl$, is only divalent, unites with only two electro-negative radicles, and does not behave like a trivalent radicle, just as much as $Co(NH_3)_6$. On the other hand, if the chlorine atom saturates a valency of the cobalt atom, it cannot be co-ordinated; for co-ordinated groups do not alter the valency of the metallic atom. In this case one can understand that the group $CoCl.(NH_3)_5$ is only divalent, but then there can be no question of an octahedral grouping, since there are only five co-ordinated groups of atoms present."

Jörgensen[4] has also pointed out that "the compound—

$$[(NO_2)_2Co.(NH_3)_2]_2C_2O_4$$

whether it be supposed to be dinitro-diammin-oxalate or dinitro-diammin-dinitro-diammin-oxalate, absolutely cannot be brought into concord with Werner's theory. He (Werner) has

[1] Werner, *Annalen*, 1902, **322**, 261. [2] *Ibid.*, 296.
[3] Jörgensen, *Zeitsch. anorg. Chem.*, 1899, **19**, 155. [4] *Ibid.*, 151.

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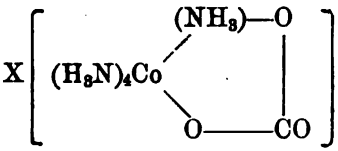
certainly tried to force[1] the salt into his system, but he has done so by assuming that C_2O_4 occupies *one* co-ordination place in the oxalo-pentammine salts, *two* such positions in the oxalato-tetrammino salts, and *four* in dinitro-diammino-oxalate. It is clear that with assumptions of this type one could prove anything."

In order to get round these and similar difficulties, Werner has to resort to formulæ[2] such as—



and to assume[3] that two molecules of water, piperidine, or of aniline can act mono-molecularly.

We have not space here to deal with the many cases mentioned by Jörgensen, which cannot, except by means of elaborate supplemental hypotheses, be brought into line with Werner's ideas. Jörgensen's papers[4] may be consulted on the subject.

Looking at the matter in its broad outlines, the following seems to be a fair summary of the chief points. In the first place, the three chlorine atoms of cobaltic chloride are evidently weakly attached to the cobalt atom. This is shown by the instability of the salt. Therefore we must conclude that the affinity of the cobalt atom is completely occupied in holding these chlorine atoms. Yet, according to Werner's ideas, the cobalt atom has still enough residual affinity left to attach to itself six ammonia molecules, and then when it has done this these molecules are so firmly hooked on by the so-called "auxiliary valencies," that they cannot be driven out of the compound as they could be from an ammonium salt. Further, the complex thus formed has apparently very much more affinity for chlorine atoms than the original cobalt atom had, as it forms a quite stable compound with them.

[1] Werner, *Zeitsch. anorg. Chem.*, 1897, **14**, 26.

[2] Werner, *Neuere Anschauungen*, p. 131. 1905.

[3] Werner, *Zeitsch. anorg. Chem.*, 1897, **15**, 243; compare Jörgensen, *ibid.*, 1899, **19**, 151.

[4] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, **5**, 147; 1897, **13**, 172; 1897, **14**, 404; 1899, **19**, 109.

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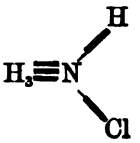
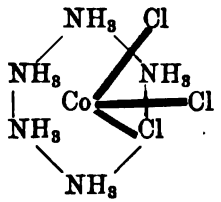
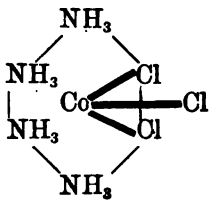
(c) *Friend's Explanation*

Friend[1] distinguishes three kinds of valency: (1) free negative valency; (2) free positive valency; and (3) residual valency. The first of these is possessed by those elements which can combine with one or more electrons; the second, positive valency, is due to a capacity for parting with an electron. Thus an element may have both negative and positive valency. Residual valency (or latent valency) differs from the others in that residual valencies can only be brought into action in pairs of equal and opposite sign. In order to distinguish between free and latent valencies, Friend represents the free ones by thick lines. For example, in ammonia the free negative valencies of the nitrogen are saturated. Now, a new negative valency can only be called out in conjunction with a positive one, so that ammonium chloride would be represented by—



Applying this view to the cobaltammines, we get formulæ of the following type—

(I.)


(II.)


Here the chlorine atoms and the ammonia molecules form a shell round the metallic atom, and are joined together by latent valencies; the ionizable chlorine in (II.) and the two ionizable chlorine atoms in (I.) are joined to the cobalt atom by free valencies.

The great advantage which this view has over both Jörgensen's and Werner's explanations lies in the fact that

[1] Friend, *Trans.*, 1908, **93**, 260, 1007; *The Theory of Valency*, p. 150. 1908.

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we have no need to assume that a chlorine atom directly attached to a metallic atom will not ionize in solution. Instead of Werner's long series of assumptions, Friend's theory requires only those which Ramsay[1] has shown to be consonant with the newer electronic views of chemical affinity.

The views of Spiegel,[2] Briggs,[3] and Arrhenius[4] resemble those of Friend to some extent; but as they do not carry the question further, we need not refer to them in detail.

(*d*) *Baker's View*[5]

According to this view, isomerism among the metallic ammines is due to difference in configuration round the nitrogen atom. The ionizable acid groups are represented as derivatives of substituted ammonias thus—

$$\rangle Co—NH_3—NH_3—X$$

The non-ionized acid groups, on the other hand, are directly united to the cobalt atom, but are prevented from ionizing by having an NH_3 group also attached to them, thus—

$$\rangle Co—X=NH_3$$

A regular series is formed in this way; as each grouping $—NH_3—NH_3—X$ is replaced by $—X=NH_3$ a single molecule of ammonia is removed, and one of the acid groups becomes non-ionizable. After the triammines, further removal of ammonia results in the substitution of the group $—X=NH_3$ by $—X=X—M$, and so complex metallo-ammonia compounds are formed.

Applying this idea to the question of the occurrence of isomeric cobaltammines, we find the following. If the symmetrical space grouping of atoms be considered as due to

[1] Ramsay, *Trans.*, 1908, **93**, 774.
[2] Spiegel, *Zeitsch. anorg. Chem.*, 1902, **29**, 365.
[3] Briggs, *Trans.*, 1908, **93**, 1564.
[4] Arrhenius, *Theorien der Chemie*, p. 78. 1906.
[5] Miss S. M. Baker, *Proc. Chem. Soc.*, 1909, **25**, 223; *Chem. News*, 1911, **103**, 162.

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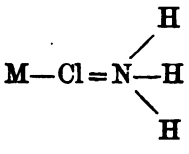
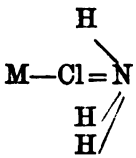
repulsion between the connecting electrons, then in the case of such a grouping as—

$$-Cl=NH_3$$

in which there is a strong attraction between the electro-positive hydrogen and the electro-negative chlorine, this attraction may overcome the repulsion of the bonds. Under such conditions there are two possible isomers—



Ex-form



En-form

which may be called *ex* and *en* according to whether the double bond is inside or outside the ring of hydrogen atoms. The possibility of such isomerism explains all the isomers which have been found among the cobaltammines. A study of their reactions makes it probable that the flavo-salts are *ex-* while the croceo-compounds are *en-* derivatives.

(*e*) *Ramsay's Views*

Ramsay,[1] in his 1908 Presidential Address to the Chemical Society, put forward the thesis that what we term an electron is really an "atom" of electricity, and from this point of view he was able to throw a new light upon many chemical problems. Before proceeding to deal with the cobaltammines, we must examine the application of Ramsay's view to the case of sodium chloride.

"If it be conceded that salt differs from its solution only in so far as the mobility of the solution permits of transfer of ions, the transfer of an electron from the sodium to the chlorine must take place at the moment of combination. Symbolized, if we write E for electron and simplify the reaction, dealing for the moment with an atom and not with a molecule of chlorine, we have—

$$ENa + Cl = NaECl$$

[1] Ramsay, *Trans.*, 1908, **93**, 774.

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Here the electron serves as the bond of union between the sodium and the chlorine.

"If it be desired to form a mental picture of what occurs, let me suggest a fanciful analogy which may serve the purpose; it is that an electron is an amœba-like structure, and that ENa may be conceived as an orange of sodium surrounded by a rind of electron; that on combination the rind separates from the orange and forms a layer or cushion between the Na and the Cl; and that on solution the electron attaches itself to the chlorine in some similar fashion, forming an ion of chlorine."

In order to save complication in formulæ, Ramsay adopts the ordinary symbol — to represent the electron, so that the above equation becomes—

$$Na— + Cl = Na—Cl$$

and on solution in water this splits up into Na and —Cl.

Turning to the case of the cobaltammine nitrites, Ramsay applies the foregoing ideas in the following manner:—

"Just as the nitrogen in NH_4Cl takes one electron from the hydrogen of the HCl and gives up one to the chlorine, so it appears reasonable to suppose that in these cobaltammines each nitrogen atom of the three ammonia groups takes from the cobalt atom one electron, whilst it gives one at the same time. The formula of the triammino nitrite would therefore be—

$$\begin{array}{c} NH_3 \\ \Downarrow \\ H_3N \rightleftharpoons Co \equiv (NO_2)_3 \\ \Downarrow \\ NH_3 \end{array}$$

If another molecule of ammonia be added, then the cobalt atom gives to the nitrogen of the ammonia an electron, but does not receive one in return. The nitrogen atom of that ammonia group is then 'over-loaded,' for it has received four electrons in addition to its normal five, making nine in all. Now, it appears that no element can be associated with more than eight in all; hence that nitrogen atom must lose an electron. This it imparts to one of the (NO_2) groups, which parts company with the cobalt atom, and, as a complex ammonium nitrite is now

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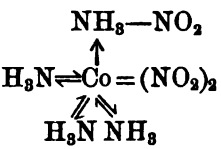
present, it is ionizable on solution in water. A glance at the proposed formula will explain the conception—



Why is the group $Co(NH_3)_3(NO_2)_3$ not ionizable? Let us first inquire: why is cobalt nitrate ionizable? (Cobalt nitrite is unknown.) Because the cobalt atom gives up an electron to each of the three NO_3— groups, remaining itself as an ion. That is, the metal cobalt has three electrons associated with it; what we call 'metallic cobalt' is a 'tri-electride' of cobalt. As 'cobaltion' it has parted with its three electrons. But, in the last of the three compounds above, the cobalt has not got three electrons at disposal; it has already parted with them to the NH_3—NO_2 groups. And we are led to conclude that in the non-ionizable compound the cobalt does not, as in its ordinary salts, part with three electrons, but that it receives them from the nitro-groups."

3. The Chemical Behaviour of the Cobaltammines

(*a*) *The Ions in Cobaltammine Solutions*

From what has been said in the previous sections, it will be evident that one of the most important questions in this division of inorganic chemistry is that which concerns the number and character of ions formed when a given cobaltammine is dissolved in water. The whole theoretical part of the subject hinges upon this point, and it is much to be regretted that up to the present time no really conclusive researches have been carried out in this direction. It is to be hoped that in the near future the problem may be attacked without *parti pris*, in order to determine at least the number of the ions in question.

Up to 1893, our knowledge of the behaviour of the cobalt-ammines in solution depended upon the work of Jörgensen and others, who deduced the number of ions in solution in the usual way from the results of chemical decompositions. In

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that year, however, Werner and Miolati[1] put forward what they call a "simple empirical rule" for determining the number of ions in solution. According to their assumptions, the number of ions in a cobaltammine solution can be measured by the conductivity of that solution, if the temperature be 25° C., and the dilution equal to one gramme molecule in a thousand litres. From this assumption they have deduced a whole series of numbers of ions which agree quite closely with what is required to fit in with Werner's hypothesis.

Attention might be drawn to one or two points. In the first place, when the results obtained at 25° C. and 1000 litres dilution agreed with Werner's views, no further measurements were made. On the other hand, when the figures obtained did not agree with the hypothesis, it was at once assumed that the substance was unstable (as in many instances was the case), and the measurements were repeated at very high concentrations and lower temperatures. In this way, of course, other figures were obtained which agreed more closely with what was required.

Further, the assumption that one can deduce the number of ions from the conductivity of a solution, cannot be regarded as incontestable. For example, in Fig. 23 is shown a series of examples in which the conductivities for 1024 litres at 25° of various salts are plotted in a line; the approximate limits of Werner's range for "di-ionic" and "tri-ionic" salts are shown by the horizontal lines. An examination of the figure will show that no sharp gradations exist, such as Werner's hypothesis requires. For instance, the conductivities of his "tri-ionic" salts lie round about the conductivity of magnesium sulphate, which is undoubtedly di-ionic, while all up the slanting line di- and tri-ionic salts alternate in a way which shows that we can deduce from conductivity alone no information with regard to the numbers of ions into which compounds dissociate.

The fact is, of course, that except in a few very restricted classes, there is no general rule connecting ionization numerically with the constitution of a compound. For example, if we take

[1] Werner and Miolati, *Zeitsch. phys. Chem.*, 1893, 12, 35; 1894, 14, 506; 1896, 21, 225.

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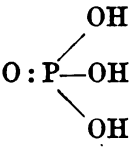
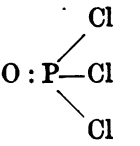
the case of phosphoric acid, it is well known that the constitution of the substance is expressed by the formula—



Now, this formula corresponds to that of phosphorus oxychloride—



and as Caven[1] has shown that the three chlorines in the latter

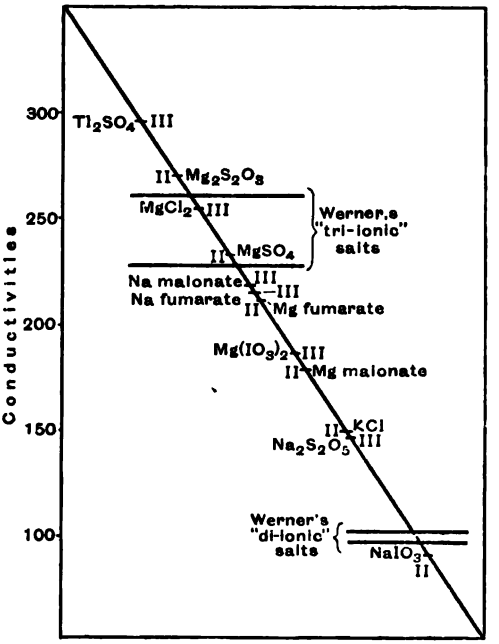


FIG. 23.

compound are equivalent to each other, we may fairly deduce

[1] Caven, *Trans.*, 1902, 81, 1362.

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that the same must be true for the hydroxyl groups of phosphoric acid, as far as *structure* is concerned. It is well known, however, that the three hydroxyl groups of phosphoric acid are *not* equivalent from the electro-chemical point of view, as with regard to methyl orange it is mono-basic, dibasic with regard to phenolphthalein, and tri-basic with yet another indicator. From this it follows that little reliance can be placed upon *à priori* connections between molecular constitution and ionization.[1]

Petersen [2] approached the matter with a much broader outlook. Taking the van't Hoff equation—

$$i = 1 + (k - 1)\alpha$$

in which k is the number of ions into which a salt dissociates, and α is the degree of dissociation of the solution, Petersen pointed out that we have two ways of calculating the approximate value of i. In the first place, we may determine the value of α in the usual way from a comparison of the conductivity at, say, v litres dilution with that at infinite dilution. The value of α_v (that is to say, the extent to which the substance is dissociated into ions when one gramme molecule is dissolved in v litres of water) is expressed by the equation—

$$\alpha_v = \frac{\mu_v}{\mu_\infty}$$

If we now substitute this value of α in the equation—

$$i = 1 + (k - 1)\alpha$$

we shall get a series of values for i if we make k equal to unity, two, three, or four. We shall thus obtain a series of four possible values for i. To distinguish which of these is the correct one, we must calculate the value of i from experimental results obtained by a different method.

Now, van't Hoff's factor i is really an expression of the ratio between the observed osmotic pressure and the calculated one in the case of an electrolyte in solution. Thus if we take an electrolyte, dissolve one gramme in 100 grammes of water, and observe the depression of the freezing-point, when

[1] Compare Walden's investigations on the relation between conductivity and degree of dissociation, *Zeit. physikal. Chem.*, 1906, **54**, 129.

[2] Petersen, *Zeitsch. physikal. Chem.*, 1897, **22**, 410; 1902, **39**, 249.

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we proceed to calculate the molecular depression we shall find it abnormal, owing to the fact that each ion acts as a molecule. To find the value of i, we must obviously divide our observed molecular depression by the normal value for water, viz. 18·7, the quotient giving the value of i.

We have now got the value of i in two ways: one possible value from the freezing-point depression, and alternative values from the conductivity measurements. We proceed to compare the freezing-point i with those obtained from the conductivity, and we shall find, of course, that the two agree only for one value of k. We therefore conclude that this value of k is the true one, and represents the number of ions in the solution in question.

An actual example will make the matter quite clear. We may take the values given by Petersen for dinitro-triammino-cobalt chloride.

v	Observed depression.	Molecular depression.	i (freezing-point).	Value of $1+(k-1)\alpha$ from conductivity measurements for $k=2$	$k=3$	$k=4$
50 lit.	0·090	45·0	2·41	1·84	2·68	3·52

Here it is obvious that the value of i found from the freezing-point agrees with that of the equivalent expression $1+(k-1)\alpha$ from the conductivity only when k is 3. Hence, under the conditions of the experiment, the number of ions in the solution is three.

Further, the accuracy of the experimental work can be controlled by the closeness of agreement between the values of i obtained in the two ways. Petersen in many cases got very close agreement between the two sets of results.

Werner and Herty[1] four years later replied to Petersen in a somewhat violent tone, admitting that theoretically his methods were perfectly accurate, but criticizing the experimental details. They gave some figures for i which did not agree with those found by Petersen. It is noteworthy that while they are extremely critical of Petersen's methods, which, after all, seem to be the best that could be devised, they give

[1] Werner and Herty, *Zeitsch. physikal. Chem.*, 1901, **38**, 331.

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absolutely no experimental details with regard to the methods they employed to obtain their own figures. Petersen [1] makes out a very strong case in his reply, and it appears strange that Werner has not given any explanation of the methods used to obtain his figures.

A comparison of the number of ions which the different workers deduce from their results in the case of several cobaltammines may be given here.[2] It shows the state of uncertainty which exists in the matter.

	Petersen.	Werner and Miolati.
Dinitrotriammino-cobalt chloride	3	2
Flavocobalt nitrate	4	2
Croceocobalt nitrate	4	2
Chloronitrotetrammino-cobalt chloride	4	3
Carbonatotetrammino-cobalt bromide	3	2

Obviously, until some definite work is done upon this branch of the subject, no conclusions can safely be drawn with regard to the number of ions in question. Two workers have arrived at conflicting results, and the question must be treated as *sub judice*. Until it is settled one way or the other, it would hardly be safe to draw conclusions from the results of conductivity methods alone.

(*b*). *The Jörgensen-Werner Controversy*

In the present section, we must consider some of the main points which came to light during the controversy between Jörgensen and Werner with regard to the constitution of the cobaltammine salts. It is, of course, quite impossible to deal even with the broad outlines of the discussion, which lasted for eight years or more; but we may select a few examples of the arguments employed on each side.

In the first place, we may mention one instance in which Werner's ideas do not appear to be capable of explaining the known facts.

If we accept Werner's octahedral arrangement of the so-called "co-ordinated groups" around the cobalt atom, it is obvious that in the case of a compound $CoX(NH_3)_5$ only one

[1] Petersen, *Zeitsch. physikal. Chem.*, 1902, **39**, 249.

[2] For further figures see Jörgensen, *Zeitsch. anorg. Chem.*, 1899, **19**, 133.

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form can exist. Now, in point of fact Jörgensen[1] has shown that in the case where "X" is a nitro-group, *i.e.* in the xantho-salts, *two* isomeric forms are known. This phenomenon Jörgensen explained by assuming that the isomerism was caused by some difference in the constitution of the two nitro-groups, and he suggested many different possible structures, the simplest of which were—NO_2 and —O.NO. Now, as will be shown later, Werner cannot admit this type of isomerism here, or he must admit it in other cases which tell against his hypothesis. But if he does not admit it here, the so-called "Co-ordination theory" offers no explanation of this isomerism.

One of the weak points in Werner's hypothesis is the ease with which it can be extended to "explain" cases of isomerism which after a time have proved to be mere mares' nests. For example, in his very first publication of his hypothesis[2] he gave an elaborate "explanation" of the occurrence of two isomeric forms of cobalt roseo-salts. Jörgensen investigated the matter, and found that no such isomerism existed. Werner[3] then declared that the views developed by him to explain the isomerism of the aquo-pentammine salts stood in no direct relation with the general ideas on the metal-ammonia compounds put forward by him, but were rather a special development, which, as regards the general ideas, was totally unimportant and totally independent, and whose fall, therefore, had no connection whatever with the main hypothesis. One might well ask why, in this case, it was worth putting it forward at all.

The crux of the whole question, however, lies in the tetrammino-salts, with which we shall now deal. In the ethylene diamine derivatives of cobalt, in which two molecules of ethylene diamine replace the four ammonia molecules of the tetrammine series, Jörgensen[4] established the existence of two isomeric series of compounds. To one of these he gave the name Praseo-salts, to the other Violeo-salts. The formula of the series would be

$$\left[\mathrm{Co}\begin{matrix}\mathrm{X}_2\\ \mathrm{en}_2\end{matrix}\right]\mathrm{X}$$

[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, **5**, 169, 172; 1899, **19**, 148.
[2] Werner, *Zeitsch. anorg. Chem.*, 1893, **3**, 301.
[3] *Ibid.*, 1897, **15**, 144.
[4] Jörgensen, *J. pr. Chem.*, (2) 1889, **39**, 17; 1890, **41**, 448.

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where "en" represents one molecule of ethylene diamine, $NH_2 . CH_2 . CH_2 . NH_2$. Now, Jörgensen found that in the case of the compounds—

$$(NO_2)_2Co(NH_3)_4X$$

which are the analogues of the ethylene diamine compounds, two isomeric substances also exist. To these he gave the names Flavo- and Croceo-salts.

Jörgensen saw that there were two possibilities to be kept in view. In the first place, the cause of the isomerism might be the same in the ethylene diamine compounds as it was in the tetrammine series; or, secondly, the origin of the isomerism in the latter case might be due to differences in the structure of the nitro-groups, just as in the case of the pentammine xantho-salts. Later,[1] he abandoned completely any idea of a parallelism between the ethylene diamine and the ammonia compounds, finding "not a single fact in support of such an assumption."

Meanwhile Werner[2] had found that when praseo-salts are warmed with sodium nitrite and dilute acetic acid, they go over into croceo-salts. Hence he deduced that croceo-salts belonged to the praseo-series, and conversely, that the flavo-salts must be violeo-compounds.

He then concludes as follows: "Since in the preparation of flavo-salts from carbonato-tetrammino chloride" (violeo-salt), "and also in the preparation of croceo-salts from praseo-cobalt chloride, intermediate tetrammino-purpureo- and tetrammino-roseo-salts" (of the composition—

a_4CoCl_2,H_2O,Cl, Tetrammino-purpureo salt
$a_4Co(H_2O)_2,Cl_3$, „ roseo „)

"are formed, it is clear that these also are present in isomeric forms. We thus obtain the following series, which correspond completely with one another:—

$\left[Co^{a_4}_{Cl_2}\right]Cl$, Praseo-salts $\left[Co^{a_4}_{CO_3}\right]Cl$, Violeo-salts

$\left[Co\ {}^{a_4}_{Cl}\ {}^{H_2O}\right]Cl_2$, Praseo-purpureo-salts Violeo-purpureo-salts

[1] Jörgensen, *Bull. de l'Acad. de Danemark*, 1895, 1.
[2] Werner, *Zeitsch. anorg. Chem.*, 1895, **8**, 182.

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$\left[\begin{matrix} a_4 \\ Co \\ (H_2O)_2 \end{matrix}\right]Cl_3$, Praseo-roseo-salts Violeo-roseo-salts

$\left[\begin{matrix} a_4 \\ Co \\ (NO_2)_2 \end{matrix}\right]Cl$, Croceo-salts Flavo-salts

Since it is proved by the above considerations that two completely corresponding series of geometrically isomeric cobalt-ammonia compounds occur, the chief problem before us is the question of the configuration of the two series." He then proceeds to deal at length with the configurations.

Jörgensen[1] draws attention to the following points: "If one now reflects that, in the preparation of croceo- and flavo-salts in the way described, the formation of isomeric (not to speak of geometrically isomeric) purpureo- and roseo-salts neither has been observed nor can be observed, and, further, that isomers most certainly cannot be 'proved' to exist by means of 'considerations,' but only by experiments, the main question is certainly, not whether the isomeric salts have one configuration or another, but rather whether such isomers exist at all.

"Werner himself has felt this, but the whole experimental proof which he adduces is the following: 'The preliminary researches'—how they are carried out is not even mentioned—'to demonstrate the existence of the isomeric tetrammino-purpureo- and roseo-salts have shown that the tetrammino-purpureo-salts of the praseo-series are deep violet, those of the violeo-series more lilac to rose-coloured; the latter go over into the former even on standing. On the other hand, the praseo-purpureo-salts are less soluble than those of the violeo-series, and the latter are converted more easily than the former into the corresponding roseo-salts.'

"Since November, 1894, when Werner wrote this, and on such shaky foundations built up whole pages of theoretical considerations with cis- and trans-forms and numerous octahedra he has found no occasion to give any further information on the subject. It therefore seems about time to prove that the whole thing is a castle in the air."

Jörgensen then goes on to give numerous experimental

[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1897, 14, 406.

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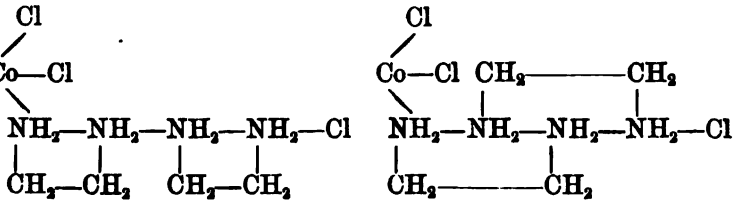
details which completely disprove Werner's assumptions; we need only quote one example. Werner takes, in the table above, praseo-chloride as his typical praseo-salt, and carbonato-tetrammino-chloride as his typical violeo-salt. Jörgensen shows that when warmed with ammonium carbonate, the former is converted into the latter. Hence either Werner's typical violeo-salt belongs to the praseo-series; or the typical praseo-salt belongs to the violeo-series.

Now, since all these difficulties arise only from the assumption that the ethylene diamine series of compounds are exactly parallel to the tetrammino-compounds, the simplest way out of the difficulty seems to be to abandon any such parallelism. Jörgensen[1] pointed out that in the case of ethylene diamine, we can imagine two possible arrangements within the cobalt-ammine molecule—



so that we might attribute the isomerism in these compounds to this difference. Now, in the ammonia compounds such an isomerism could not occur, owing to the similarity of all four ammonia groups. We should therefore expect to find no isomerism in the case of the ammonia-compounds of the type $[(NH_3)_4CoCl_2]$; and, as a matter of fact, no such isomers are known, the compound exists in one form only. But as soon as we replace the chlorine atoms by nitro-groups, producing $[(NH_3)_4Co(NO_2)_2]$ we introduce the possibility of structural isomerism again in the nitro-groups, and in this case we actually find two isomers.

It seems, therefore, unnecessary to assume the existence of ammonia-violeo-salts until some better evidence is produced.[2]

Werner[3] has endeavoured to disprove Jörgensen's assumption of isomerism in the nitro-groups of the tetrammino-salts by the following work.

[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1897, 14, 410.
[2] *Ibid.*, 1899, 19, 146.
[3] Werner, *Ber.*, 1901, 34, 1710.

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Jörgensen [1] had shown that when the two isomeric dinitrito-tetrammino-chlorides

$$\left[\begin{matrix}(NO_2)_2\\ Co\\ (NH_3)_4\end{matrix}\right]Cl$$

are treated with hydrochloric acid, one isomer loses *one* nitro-group, while the other loses both at once. From this behaviour, Jörgensen deduced that the two nitro-groups were differently constituted in the tetrammino-compounds, and suggested as one possibility that in the one salt the group might be present as $—NO_2$, while in the other it might be —O . NO, just as in the case of the pentammine salts.

Werner, assuming the parallelism between tetrammino- and diethylenediammino-compounds which Jörgensen had proposed and subsequently abandoned, owing to the weight of evidence against it, postulated that this isomerism of the nitro-groups must also occur in the corresponding diethylene diammino-compounds, whose formulæ would thus be—

$$\left[\begin{matrix}O\,.\,NO\\ \diagdown\\ Co—NO_2\\ \diagup\\ en_2\end{matrix}\right]X \qquad \left[\begin{matrix}O\,.\,NO\\ \diagdown\\ Co—O\,.\,NO\\ \diagup\\ en_2\end{matrix}\right]X$$

Werner found that, when acted on by nitric acid, both salts lost one nitro-group and were converted into nitrito-nitrato-compounds, which on treatment with hydrochloric acid in aqueous solution give identical chloro-nitrito-salts.

If this chloro-nitrito-salt is to be derived from both the above dinitrito-compounds, it must, according to Werner, have the following constitution :—

$$\text{(I.)}\left[\begin{matrix}O\,.\,NO\\ \diagdown\\ Co—Cl\\ \diagup\\ en_2\end{matrix}\right]X$$

Now, there is another chloro-nitrito-salt known, isomeric with this ; and if the difference lies in the structure of the nitrite

[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1899, 19, 109.

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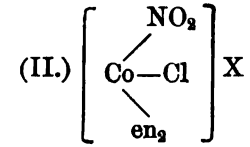
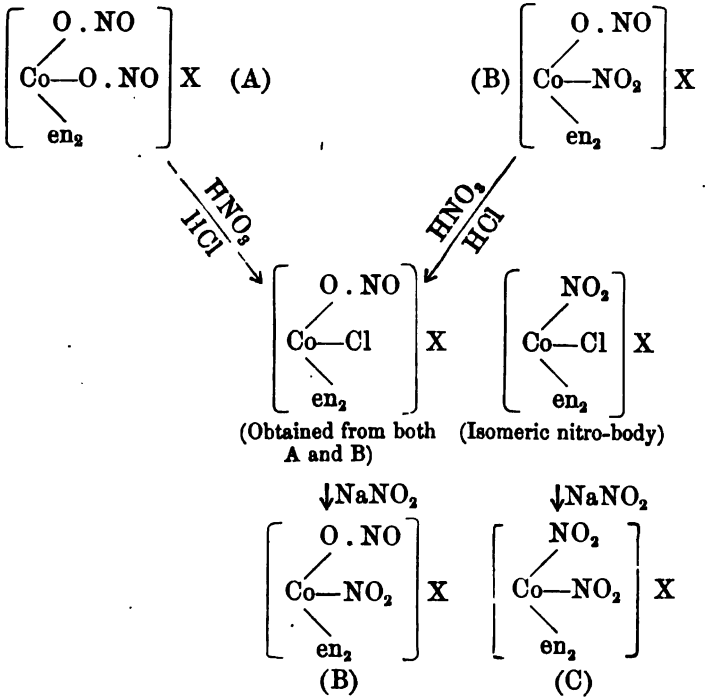
group, this new chloro-nitrito-compound must have the constitution—



this is, it must have a nitro- instead of a nitrito-group.

When treated with sodium nitrite, this substance gives quantitatively the dinitrito-compound, in which the two nitro-groups were assumed originally to be alike; while the compound (I.) under the same conditions gives the isomeric dinitrito body in which the two nitrito-groups were different in behaviour. These changes are shown in the scheme below. It will be seen that instead of the compound (A) being regenerated, we get a compound (C).



The chief points to notice in regard to this reasoning are as

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follows: In the first place, it assumes the parallelism between the tetrammino-compounds and the diethylene-diammino-compounds. In the second place, it assumes that the isomerism of the ethylene-diamine compounds has its origin in the nitro-groups, and not, as Jörgensen suggested, in the arrangement of the ethylene-diamine groups within the molecule. Thirdly, it assumes that under the strenuous treatment to which the nitrite groups are exposed during the above series of reactions, no desmotropic change in their constitution takes place.

The question at issue is quite clear. Jörgensen points out that if we take the three cases of the dichloro-diethylene-diammino salts, the dinitrito-tetrammino-salts, and the dichloro-tetrammino-salts, two isomeric series are known in the case of the first two sets, but the dichloro-tetrammino-compounds occur in one form only—

$\left[Co\begin{smallmatrix}Cl_2\\en_2\end{smallmatrix}\right]X$ Occur in two forms.

$\left[Co\begin{smallmatrix}(NO_2)_2\\(NH_3)_4\end{smallmatrix}\right]X$ Occur in two forms.

$\left[Co\begin{smallmatrix}Cl_2\\(NH_3)_4\end{smallmatrix}\right]X$ Only one form known.

So that in each case where isomerism is observed there are either two nitro-groups or two ethylene diamine molecules. Where these are both absent, no isomerism occurs. Werner, on the other hand, maintains that his theory accounts better for the facts, though he has not been able to produce the two isomeric tetrammino-salts which, according to his views, ought to exist. The non-production of these salts is specially significant when we consider how easily we can transform one diethylene-diamine isomer into the other; evaporation with mineral acids produces one form, from which the other can be regenerated by evaporating with water after making the solution neutral.

4. Conclusion

We have now surveyed the chief hypotheses which have been put forward to account for the isomerism and behaviour

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of the various cobaltammines; and from the contents of the foregoing sections it is clear that the whole question is at present in a very unsettled condition. The explanations we have mentioned may be divided into three classes: first, those based upon the electron theory; secondly, those which postulate new ideas of valency; and lastly, explanations founded on the old ideas of valency.

Though it seems evident that eventually the electron theory will be brought into close connection with chemistry through the common ground of physical properties, the time has not yet come for putting it to the test of experiment in the case of the cobaltammine compounds. We shall require to amass a very large quantity of experimental material in other branches before we can hope for experimental proof in this particular section of the subject. Our experimental methods in this field lag far behind the theoretical developments which we can foresee, and our hypotheses in this region must remain merely hypotheses for some time to come.

Friend's views form in a way a bridge between the electronic view and the older and more purely chemical conceptions of valency. The only point to which objection might be taken is their application to the case of substances containing non-ionizable nitro-groups or sulphate radicles, for in these cases the formulæ would be somewhat complicated. The chief advantage of this explanation lies in the fact that it evades the assumption that a halogen atom directly attached to a cobalt atom does not become ionized in solution.

Baker's views have the same advantages as Friend's; but in this case also the nitro-groups and sulphate radicles complicate the formulæ.

Turning now to Werner's ideas, we have already mentioned some cases in which they do not fit the experimental results; but the deficiencies of the so-called "Co-ordination theory" can easily be seen if we examine one of the simplest cases to which its inventor has applied it, viz. that of ammonium salts.[1] Here we are asked to assume that the reaction between ammonia and an acid takes the following course:—

$$H_3N \quad + \quad H.I = H_3N \ldots H.I$$

[1] Werner, *Annalen*, 1902, **322**, 261.

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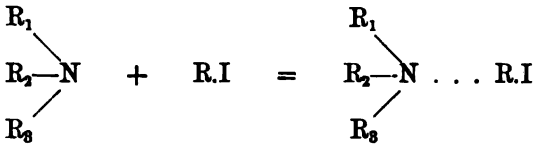
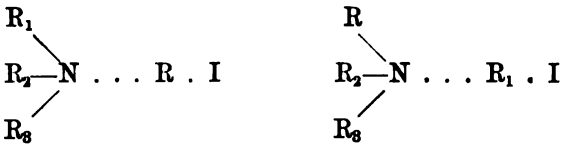
Now let us take the perfectly analogous case of the addition of an alkyl iodide to a substituted ammonia—



According to this idea, the group R would be attached to the nitrogen atom in a fashion different from that in which the other groups R_1, R_2, and R_3 are attached. This is, of course, quite absurd; for in that case we should get two isomeric compounds by starting in the one case from R_2R_3R . N and R_1 I, and in the other case from $R_1R_2R_3$. N and R . I. The two end-products would be in these cases—



As was shown by Jones,[1] such isomers are not formed, the end-products being the same from each process.

The only other assumption we could make is to suppose that in the ammonium salt all four groups R, R_1, R_2, R_3, are "co-ordinated" with the nitrogen atom.* This leads us to the following conclusion. Since the groups R_1, R_2, R_3 in the ammonium salt have the same properties as the same groups in the tri-substituted ammonia N . $R_1R_2R_3$, it is obvious that in the latter case they must be "co-ordinated" also. (The only other possible assumption is that a so-called "auxiliary valency" is the same as a "main valency.") But if they are "co-ordinated" to the nitrogen atom in the case of the molecule N . $R_1R_2R_3$, that atom cannot be trivalent; and so we shall have to throw over all the ideas upon which our present-day chemistry rests, merely for the sake of adopting Werner's

[1] Jones, *Trans.*, 1905, 87, 1721.

* This new view (which, of course, clashes with the other) has been advanced by Werner in the second edition (1909) of his *Neuere Anschauungen*, p. 211. It furnishes another example of the elasticity of the Wernerian hypothesis, and the ease with which it can be modified to get round a difficulty.

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hypothesis. Of course it is quite possible that the difficulties mentioned above might be got round by means of elaborate supplementary postulates; but since in the end they get us no further forward than we can go with our ordinary assumption of change of valency from three to five, it seems unnecessary to take the long road when we can find a much more direct one. From the electro-chemical point of view, Arrhenius [1] has adduced further evidence, which, according to him, proves "the inadequacy of Werner's theory" of ammonium salts.

Finally, we come to the Blomstrand-Jörgensen theory, which is based upon the old and well-tried theory of valency. As Jörgensen has shown,[2] this theory can be brought into agreement with all the facts known up to the publication of his last paper on the subject. Since that time Werner has published his research on the dinitro-diethylenediammino compounds to which we referred in our last section, and there the matter rests.

[1] Arrhenius, *Theories of Chemistry*, 1907, pp. 82–88, 88.
[2] Jörgensen, *Zeitsch. anorg. Chem.*, 1899, 19, 109.

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CHAPTER X

THE ELEMENTS OF THE RARE EARTHS

1. Introductory

In the fourth column of the Periodic Table is a group of substances whose atomic weights lie between 180 and 130. These substances, together with scandium and yttrium, make up the greater part of what are termed the rare earths. These rare earths are found for the most part in the Scandinavian peninsula, but deposits have also been brought to light in the Ural Mountains, and in certain parts of America and Australia. It appears that rare earths are usually found among eruptive rather than among sedimentary deposits, and that they are most likely to occur in archæan rocks, particularly in granite.

The rare earths are chiefly made up of a series of basic oxides, but it is usual to divide them into three groups: the cerium group, the terbium group, and the ytterbium group. This division is somewhat arbitrary, for the rare earth elements appear to resemble each other very closely indeed, and we have really a single series of substances with properties changing slightly as we pass from member to member, rather than three groups whose properties differ sharply from each other. Still, for the sake of convenience, the following arrangement is usually employed :—

Cerium group.		Terbium group.		Ytterbium group.	
Element.	Atomic weight.	Element.	Atomic weight.	Element.	Atomic weight.
Scandium	44·1	Europium	152·0	Dysprosium	162·5
Yttrium	89·0	Gadolinium	157·3	Holmium	?
Lanthanum	139·0	Terbium	159·2	Erbium	167·4
Cerium	140·25			Thulium	168·5
Praseodymium	140·6			Neo-Ytterbium	172
Neodymium	144·3			Lutecium	174
Samarium	150·4				

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2. The Importance of the Rare Earths

The group of the rare earths has very considerable importance, whether we look upon the question from the point of view of theory or from the practical standpoint. With the theoretical problems involved we shall deal in the final section of this chapter, so we need not enter here into the question of the position which must be assigned to these elements in the Periodic System.

On the practical side, the rare earths were without any importance until a quarter of a century ago; but in 1884, Auer von Welsbach took out a patent in which the present-day incandescent gas mantle was foreshadowed, and at once the question of the rare earths became a commercial one. At that time the known deposits were limited, both in extent and capacity, and it consequently became questionable whether the raw material for the manufacture of mantles could be produced at a price sufficiently low to allow of commercial success. Fortunately, large deposits of monazite sand were soon afterwards discovered in Carolina and in Brazil. These beds rendered it possible to obtain the rare earths comparatively cheaply, and the incandescent gas-lighting industry has grown upon them.

At this point the theoretical side has shared in the profit, for the mantle industry has produced vast quantities of bye-products which have been placed at the disposal of investigators, who would otherwise have been forced to work up the crude material for themselves at the cost of much time and labour. At the present day, these bye-products form one of the most fruitful sources in the investigation of the elements of the rare earth series.

3. The Physical Properties of the Rare Earth Elements

Muthmann and Weiss[1] have carried out a comparison between some of the members of this group of substances, and have obtained the following results.

As regards colour, lanthanum is a white metal similar to tin

[1] Muthmann and Weiss, *Annalen*, 1904, **331**, 1.

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in appearance; cerium is rather more like iron; neodymium shows a faint tinge of yellow; while praseodymium is more pronouncedly yellow in tint.

When the hardness of these elements is compared with that of lead, tin, and zinc, they lie in the following order: lead, tin, cerium, lanthanum, zinc, neodymium, praseodymium. Samarium is harder than any of the foregoing.

The melting-points are shown in the following table. Aluminium melts at about 660° C., and silver at about 960° C., which gives a rough standard of comparison—

	M.P.
Cerium	623°
Lanthanum	810°
Neodymium	840°
Praseodymium	940°

The specific gravities of the four substances are—

Lanthanum	6·15
Praseodymium	6·48
Neodymium	6·96
Cerium	7·04

Cerium, therefore, has about the same density as tin (7·3).

By means of a Berthelot-Mahler calorimeter, Muthmann and Weiss investigated the heats of combustion of these substances, comparing them with aluminium and magnesium. The results are given in the table below :—

One gramme	gives	Heats of formation per molecule.	
Mg	5870·8 cal.	3MgO	429·0 cal.
Al	7140·0 ,,	Al_2O_3	385·6 ,,
Ce	1603·2 ,,	$1\frac{1}{2}CeO_2$	336·9 ,,
Pr	1466·8 ,,	Pr_2O_3	412·4 ,,
Nd	1506·0 ,,	Nd_2O_3	435·1 ,,
La	1602·1 ,,	La_2O_3	444·7 ,,

4. The General Chemical Character of the Rare Earth Elements

The metals of the rare earths are comparatively reactive, and enter into direct combination with various elements. They burn in air, giving rise to oxides of the type Me_2O_3; but in addition to this series, some of the metals can be converted

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into oxides having the composition MeO_2. For example, cerium oxide of the formula Ce_2O_3 is unstable, the stable oxide being CeO_2. The corresponding oxide of praseodymium has also been isolated, but it is much less stable than the cerium one. Terbium and neodymium also yield higher oxides having the compositions TbO_2 and NdO_2. It is a curious fact that there are two forms of the oxides Me_2O_3, one form being prepared by heating the nitrate of the metal, the other form being obtained by igniting the hydroxide. The two varieties are different in both physical and chemical properties. It appears likely that this case is parallel to that of the two forms of calcium oxide (unslaked lime and overburned lime) and to the two varieties of magnesium oxide. The origin of the difference in properties very probably lies in the existence of two different polymeric forms of the oxides.

The oxides of the rare earth metals are bases of medium strength; the order of basicity appears to be the following, the strongest bases being placed first:—

$$La_2O_3,\ Pr_2O_3,\ Nd_2O_3,\ Ce_2O_3,\ Y_2O_3,\ Sm_2O_3,\ Gd_2O_3,\ Tb_2O_3,$$
$$Ho_2O_3,\ Er_2O_3,\ Tm_2O_3,\ Yb_2O_3,\ Sc_2O_3,\ CeO_2$$

The behaviour of ignited lanthanum oxide resembles that of quicklime; it hisses when placed in contact with water, and absorbs carbon dioxide from the air. The oxides of the ytterbium series are much less active in this respect. From the fact that their salts with strong acids are not measurably hydrolyzed even in dilute solution, it follows that the oxides of the cerium group are the strongest bases derived from trivalent elements.

The rare earth metals combine directly with hydrogen and nitrogen as well as with oxygen. The hydrides have the general formula MeH_2 or MeH_3, and are obtained either by passing hydrogen over the metals at 200° C. to 300° C., or by the action of magnesium upon the metallic oxides in a stream of hydrogen. The nitrides are formed by the action of nitrogen upon the oxide in presence of magnesium, or from the carbides by the action of ammonia. They have the composition MeN.

The carbides of the rare earth series have the general

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formula MeC_2. They are produced by the electrolytic reduction of the oxides in presence of carbon.

It is unnecessary for us to enter into details with regard to the salts of these metals. They present no special characteristics. The rare earth elements form salts with nearly all the ordinary organic and inorganic acids, and these salts possess to a great extent the ordinary properties of salts of strong bases.

5. Methods of Preparing and Purifying the Rare Earths

In the present section no attempt will be made to enter into any great detail in the description of the various methods employed to divide the rare earths from the minerals among which they occur, and to separate the elements of this group from one another. For these details the reader is referred to larger treatises.[1] All that we can do in this place is to indicate briefly the main lines of the separations, choosing as far as possible the more characteristic of these.

There are four chief stages in the isolation of the rare earths from the deposits in which they occur naturally—

A. The decomposition of the mineral and the isolation of the rare earth class.

B. The conversion of the rare earth oxalates into soluble salts.

C. The separation of the rare earth group into three sub-groups by means of double salt formation with potassium sulphate.

D. The isolation of the various elements from the cerium, terbium, and ytterbium sub-groups.

Section D we cannot enter into, as each element requires special methods for its treatment. We shall content ourselves with indicating in outline the principles underlying the methods actually employed.

A. In nature, the rare earths occur among silicates, which are usually easily broken up by evaporating the ore to dryness with concentrated hydrochloric or sulphuric acid. The powdered

[1] Abegg, *Handbuch d. anorgan. Chem.*, 1906, vol. iii.; Moissan, *Traité de chimie minerale*, 1904, vol. iii.; Dammer, *Handbuch d. anorgan. Chem.*, vol. iii. (1893), vol. iv. (1902); Browning, *Introduction to the Rarer Elements* (1909).

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residue is then added to water, and any insoluble portion is filtered off. The solution now contains the rare earths in the form of chlorides or sulphates, and may also contain salts of copper, bismuth, molybdenum, and iron. Thorium also is often present. The solution is treated with sulphuretted hydrogen to precipitate the metals of the second group. This leaves us with the rare earth elements, iron, and thorium in the solution. After oxidation of the ferrous iron to ferric with chlorine, we add a little hydrochloric acid, and then precipitate the rare earth elements and thorium in the form of oxalates.

B. Since the oxalates are insoluble substances, we must convert them into some other salts which we can get into solution. This is usually done by one of three methods. The oxalates may be heated to form oxides, from which any required salt can be produced; or we may simply dissolve the oxalates in hot nitric acid, and thus obtain the easily soluble nitrates; or, finally, we may boil the oxalates for a considerable time with caustic potash solution, which gives us the hydroxides, and from these we can produce any salt we may need. At this point we have to get rid of the thorium which still remains in the solution. This is usually done by adding hydrogen peroxide to the nitrate solution; after warming, a precipitate of thorium peroxide separates out and is filtered off.

C. We have now to separate the rare earth salts into three main groups by means of double salt formation with potassium sulphate. It has been found that in this way we get the following classification:—

1. Elements giving practically insoluble double salts: Scandium, cerium, lanthanum, praseodymium, neodymium, didymium, and samarium.
2. Elements giving soluble double salts: Europium, gadolinium, and terbium.
3. Elements giving easily soluble double salts: Dysprosium, holmium, erbium, thulium, yttrium, ytterbium.

Instead of potassium sulphate, sodium sulphate is sometimes used.

D. When we come to the actual isolation of one element of the rare earth series from its companions, there are two chief methods which we may employ. The first of these depends upon the basicities of the different metals; the second upon

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the differences in the solubility of their salts. The former method is capable of subdivision; for we may depend either upon a fractional precipitation of the salts by means of bases of different strengths, or we may reply upon a differential decomposition of the nitrates by means of heat. We must now give an outline of these methods.

1*a*. The principle underlying the method of fractional precipitation is almost self-evident. If we take two substances X and Y in solution, and add to them a third substance Z which is capable of precipitating both X and Y, then if we add excess of Z, both X and Y will be completely deposited from the solution. If, on the other hand, we add a quantity of Z which is insufficient to precipitate the total quantity of X and Y present, it is clear that the amounts of X and Y precipitated will depend to a great extent upon their chemical behaviour with respect to Z. Suppose that Z is a base which is very much stronger than A, but only very little stronger than B. If we have one molecule of each body present, it is clear that Z will displace A from its salts rather than B. Consequently we shall have A precipitated and B left in solution. In the case of the rare earths, this method is employed, using such bases as ammonia, magnesia, caustic potash, caustic soda, or organic bases. In the first precipitation the substance is separated into two parts: precipitate and mother liquor. The precipitate is then redissolved, and the process is repeated. The crystals resulting from the second fractional precipitation are once more dissolved and fractionally precipitated, and the process is continued until a pure substance is obtained.

1*b*. The second method, depending upon the difference in basicity of the various members of the rare earth group, is carried out in the following manner. In the first place, the mixed oxalates are converted into nitrates in the usual way, and to this mixture is added some alkali nitrate in order to lower the melting-point of the whole mass. Thereafter the mixture is fused. It is then found that the nitrates decompose, and usually the most negative oxide separates out first. This is removed from the mass by solution, and the process repeated again and again as in the last case.

2. The method depending upon the solubilities of the salts of the rare earths is simply a process of fractional crystallization.

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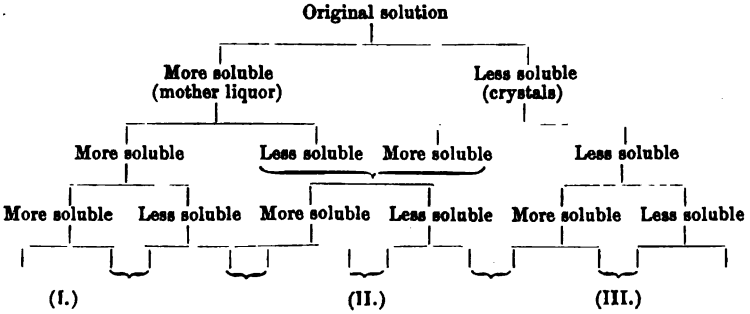
The mixture of salts is dissolved in water, and the solution is then evaporated until about half the solid separates out. This is filtered off and dissolved in water, and the same process is repeated. At the same time the mother liquor is again evaporated till half its solute separates out, and the process is repeated a sufficient number of times. Where there are more than two elements present, it is usual to mix the fractions in the following manner. After the first crystallization, we have crystals (A) and mother liquor (B). In the second set of crystallizations, each of these gives rise to a set of crystals and a mother liquor. The crystals derived from the second crystallization of the mother liquor (B) are then mixed with the mother liquor derived from the recrystallization of (A), and in this way a third set of fractions is produced which grow more and more rich in the salts whose solubilities lie between the two extremes. The scheme below will make the point clear



The brackets indicate that two fractions have been mixed together before recrystallization.

A glance at the scheme will show that we are accumulating the more soluble salts at (I.), the salts of intermediate solubility at (II.), and the least soluble salts at (III.).

The salts which have been found most useful in this method of separation are the chromate, sulphate, nitrate, oxalate, and formate. The metallic derivatives of acetylacetone have also been utilized. James [1] has recently discovered two methods by means of which rapid separations of the yttrium earths can be carried out. In the first of these, the rare earth oxalates

[1] James, *Chem. News*, 1907, **95**, 181; 1908, **97**, 61, 205; *J. Amer. Chem. Soc.*, 1907, **29**, 495. See also *Ibid.*, 1908, **30**, 979, for his general scheme of separation.

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are dissolved by warming them with a saturated solution of ammonium carbonate in dilute ammonia; and the fractionation is carried out by simply boiling the solution until a precipitate is thrown down. If five fractions of approximately equal weight be obtained in this manner, the first contains yttrium, the second is mainly holmium and dysprosium, the third is a mixture of various elements, while the last two contain erbium. James' second method depends upon the fractionation of the bromates of the rare earths; he obtains these from the corresponding oxalates by treating the latter with sulphuric acid, and then with barium bromate.

Now, let us suppose that we have carried out a series of fractional precipitations or crystallizations. The question at once arises: Have we carried the process to its end and secured the pure product we set out to obtain? In order to answer this question, we must know whether or not we are altering the composition of our substance in the course of the fractionation. Thus quite early in the series of fractionations it becomes advisable to find out what change each successive operation produces in the substance under treatment.

There are two methods by means of which we may settle the question. If we are gradually purifying a crude substance, it is obvious that if, after each operation, we determine the equivalent of the metal (or the average equivalent of the mixture in the first case) we shall get a gradual approximation to the equivalent of the pure metal, as the fractions contain less and less impurity the further the process is continued. For example, if we start with a mixture of cerium and lanthanum, the equivalent of the mixture (if the two metals be present in equal proportions) will lie halfway between those of cerium and lanthanum. As our fractions become richer and richer in cerium, the equivalent of the fraction will draw closer and closer to the cerium equivalent; and when the fraction contains nothing but cerium salt, we shall, of course, find the equivalent of cerium. This method is very rough at the best; and when applied to the case of the rare earths it is unsatisfactory, owing to comparatively small differences between the equivalents of the various metals in the group.

The second method, which is much more refined, consists in applying the spectroscope to the problem. Here we have a

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considerable choice of procedure, for we may employ either absorption spectra or emission spectra, and in the latter class we have three different types: spark spectra, arc spectra, or phosphorescence spectra. The principle of the method is similar to that dealt with above. The spectrum of each set of fractions is examined, and purity is counted as attained when repeated fractionation fails to alter the spectrum.

6. The Place of the Rare Earth Elements in the Periodic System

An examination of the form of the Periodic Table which is given in most text-books will show that the elements of the rare earths (excluding scandium and yttrium) lie just at a point in the tables where a considerable number of blank spaces occur: to the right of them lie eight gaps in columns V., VI., VII., and VIII., while to the left of them are seven other blanks in the table, under xenon, cæsium, silver, barium, cadmium, lanthanum, and indium. If an attempt be made to fit the rare earth elements into the table in the usual way, it will be found that they cannot be arranged in any satisfactory manner. The problem of the position in the Periodic Table which must be assigned to these bodies is one of some complexity, and it is not astonishing that several investigators[1] have endeavoured to solve it.

Up to the present time attempts have been made to arrive at a solution from three different points of view. In the first of these, it is assumed that the rare earth elements are all trivalent and can be placed in the third group of the Periodic System. The second view is based upon the arrangement of these elements (like the others in the system) in the order of their atomic weights, and under this classification they fall into Groups IV., V., VI., VII., and VIII. The third explanation is based upon the assumption that the elements of the rare earths form a bridge between lanthanum and tantalum; and a further development of this idea by Crookes has led to a new conception

[1] Brauner, *Zeitsch. anorgan. Chem.*, 1902, **32**, 1; *Verh. d. deutsch Naturforscher u. Aertste*, 1899, II., 131; Retgers, *Zeit. physikal. Chem.*, 1895, **16**, 661; Steele, *Chem. News*, 1901, **84**, 245; Biltz, *Ber.*, 1902, **35**, 562; Reychler, *Les théories physico-chimiques*, 1903, p. 50; Rudorf, *Zeitsch. anorgan. Chem.*, 1908, **37**, 177.

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of the nature of chemical elements. We shall take up these three main hypotheses in turn, and briefly review the evidence which bears upon each of them.

The view that all the rare earth elements should be placed in the third column of the Periodic Table is one which has the major part of the practical evidence in its favour, though some facts cannot be brought into line with it. With the exception of cerium, the rare earth metals in their commonest forms appear to be trivalent, and on this ground they should occupy a position in the same group as scandium, yttrium, and lanthanum. Against this view we may urge the objection that there is no room for this series of substances in that position in our present Periodic System; while the exclusion of cerium from the third group would produce a hiatus in the table which would very much diminish the symmetry which is its chief recommendation.

If we suppose that these elements do not belong to the third group of the table, we have two other possibilities before us; for we may assume that the rare earths are distributed through the table in the order of their atomic weights, just as the other elements are, or we may place them in a class by themselves, in which case we shall have to modify the Periodic Table in some way.

Let us take the first of these possibilities and see to what conclusions it leads us. The point will be best understood if we compare two series, the fourth and the eighth in the table. The eighth series is, of course, arranged on the assumption that the elements are to be placed in the order of their atomic weights.

Group.	0.	I.	II.	III.	IV	V.	VI.	VII.	VIII.			
Oxide .	—	R_2O	R_2O_2	R_2O_3	R_2O_3	R_2O_3	R_2O_3	R_2O_3	R_2O_3			
Series 8	Xe 128	Cs 132·8	Ba 137·4	La 139·0	Ce 140·2	Pr 140·6	Nd 144·3	Sm 150·4	Eu 152	Gd 157·3	Tb 159·2	Ho ?
Series 4	A 39·9	K 39·1	Ca 40·1	Sc 44·1	Ti 48·1	V 51·2	Cr 52·1	Mn 54·9	Fe 55·8	Co 58·9	Ni 58·7	Cu 63·6
Highest oxide	—	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8	R_2O_4	R_2O_4	R_2O_3

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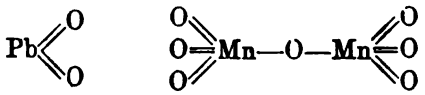
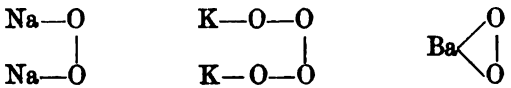
It is known that lanthanum, cerium, praseodymium, and so forth, have the faculty of forming oxides of the type R_2O_3, and to this extent they resemble the series scandium, titanium, vanadium, etc.; but if we are to push the analogy between the two groups to its full extent, we must be prepared to compare the higher oxides as well as the lower ones. In the last line of the table above, we have placed the highest type of oxide corresponding to each of the elements in the fourth series, and the question now arises: Have we any evidence of the occurrence of analogous oxides in the case of the rare earth elements which we have placed in the eighth series? As Brauner[1] has pointed out, the problem is complicated by the occurrence of two different types of peroxides (Schönbein's ozonides and antozonides). The "ozonides" or polyoxides contain their oxygen in the form of atoms doubly linked to the metal or bridging the gap between two metals:—



while the superoxides or "antozonides" contain the group —O—O—



The difference between the two is best seen in their behaviour towards dilute acid. The polyoxide is not usually attacked by dilute acid, and when it is attacked the products are oxygen and water in addition to the salt of the acid used; the superoxide, on the other hand, yields hydrogen peroxide. It is clear that evidence as to the valency of the metal deduced from an examination of its peroxide can be relevant only if we are dealing with a polyoxide. The superoxide type throws no certain light upon the point.

Unfortunately, in the case of the rare earth series, the properties of the peroxides are but little known at the present day, and consequently we are without definite evidence with regard to their constitution. Until we know with certainty whether a

[1] Brauner, *Zeit. anorgan. Chem.*, 1902, **32**, 1.

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given peroxide is a member of the superoxide or the polyoxide class, we cannot lay much stress upon any deductions with regard to valency which we may base upon this particular substance.

From the results of his researches, Brauner has come to the conclusion that there is not sufficient evidence to allow the assumption that praseodymium, neodymium, and their followers yield the same type of peroxides as is formed by vanadium, chromium, etc.

Again, the properties of the rare earth elements do not lie halfway between those which would lie above and below them in the columns in which we have placed them. One example will suffice. It will be remembered that the specific gravity of any element in a group of the Periodic Table usually approximates to the mean of those above and below it, but when we compare neodymium's specific gravity and colour with those of molybdenum and tungsten, between which it would lie if this arrangement of the table were correct, we find that the rule does not hold.

	Specific gravity.	Colour.
Molybdenum	8·6—9	Silver-white
Neodymium	6·96	Yellow
Tungsten	19	Steel-grey

In the case of the other metals, such as those lying in the eighth group, the resemblance of the rare earth element to its neighbours is even less apparent.

It therefore seems doubtful whether this view of the place of these bodies in the Periodic System can be maintained, and it seems most probable that as our knowledge of the group increases we shall be less inclined to adopt this form of classification. There remains still to be considered the question of placing these substances in a class by themselves.

Brauner has suggested that since, in the ordinary Periodic Table, there is no room for us to arrange the rare earth group, we must expand the table into a three-dimensional figure. On this assumption, cerium and its followers would form a horizontal bridge between two vertical planes containing the other elements, or they would be arranged upon a plane perpendicular to those containing the other elements. The table on p. 189

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Series.	Group 0.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.			
1	—	1 H	—	—	—	—	—	—	—			
2	He 4	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	—			
3	20 Ne	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35·5 Cl	—			
4	A 40	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 59	Cu 63
5	—	63 Cu	65 Zn	70 Ga	72 Ge	75 As	79 Se	80 Br	—			
6	Kr 82	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	– 100	Ru 102	Rh 103	Pd 106	Ag 108
7	—	108 Ag	112 Cd	114 In	119 Sn	120 Sb	128 Te	127 I	—			
8	Xe 128	Cs 133	Ba 137	La 139	Ce 140	Pr 140·5	Nd 144	—				
					—	Sm 150	Eu 152	—				
					Gd 157	Tb 159	Dy 162·5	Ho ?				
					Er 167	Tm 168·8	Yb 172	Lu 174				
					– 178	[illegible]82	W 184	– 190	Os 191	Ir 193	Pt 195	Au 197
9	—	197 Au	200 Hg	204 Tl	207 Pb	209 Bi	212 –	214 –	—			
10	– 218	– 220	Ra 226	– 230	Th 233	– 235	U 239	—	—			

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shows Brauner's arrangement,[1] the part printed in heavy type being supposed to lie perpendicular to the plane of the paper, while the section containing tungsten and its successors is supposed to lie above and parallel to the plane of the page. The table has been modified from Brauner's in order to bring it into line with the 1909 Table of Atomic Weights.

In his Presidential Address to the Chemical Society in 1888, Crookes[2] put forward a view of the rare earths which now, after twenty years, seems capable of throwing very considerable light upon researches which have been carried out in other branches of chemistry since it was published, while its applicability to the rare earth problem has become even stronger than ever. Without extensive quotation it would be impossible to do justice to Crookes' conceptions, but the following summary will show the general trend of the argument as far as it concerns the rare earths.

Crookes introduced into chemistry the conception that what we are accustomed to treat as elements are not really homogeneous bodies, but are to be regarded rather as aggregates of particles which differ from each other to some extent, though when taken in large groups their mean characteristics correspond to those of our so-called elements. We may make this clear by a concrete example. Suppose that we had a crowd of men of different nationalities, British, Japanese, Negroes, and Polynesians. If we were asked to classify these, we should have no difficulty in separating them into four different groups, and in the mass each group would show its distinct racial characteristics. But if we then examined the members of each group, we should find that each individual differed to some extent from his neighbour. In the British group the native of Devonshire would differ from the Cockney and from the Yorkshireman, and yet we should have no doubt about his nationality. Crookes applied similar ideas to chemical elements, and suggested that up to the present time we have only got to the stage of separating particles into chemical nations.

Let us carry the analogy a stage further. Let us suppose

[1] Brauner, *Zeit. anorgan. Chem.*, 1902, **32**, 18.

[2] Crookes, *Trans.*, 1888, **53**, 487; see also *Trans.*, 1889, **55**, 257 ff. The reader is recommended to consult these papers, the first of which is full of very valuable and striking views.

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that the British group of men represents the rare earth family of elements. Just as the elements of this class resemble each other much more closely than chlorine resembles bromine, so the Devonshire member of the British group will be more like the Yorkshireman than a Japanese is like a negro. Crookes thus introduces a new class of bodies, which he terms "meta-elements." These meta-elements resemble each other very closely, much more closely than one ordinary element resembles another; they have many properties in common, and the separation of the meta-elements from each other is much more difficult than the separation of two ordinary elements. This, on Crookes' view, is due to the fact that in the meta-element the particles do not resemble each other as individuals to the same extent as is the case in the ordinary elements. In the case of chlorine, the factor which we call atomic weight is represented by the figure 35·5. Here the great bulk of the component atoms may be supposed to have this atomic weight; a small percentage may vary from this figure to the extent of a decimal place, while a few others may stray as much as a whole number or two on one side or other of the mean. The ultimate atoms whose factor is not exactly 35·5, but a little higher or lower than 35·5, will congregate round the 35·5 nucleus, forming a group whose average value will be 35·5. In like manner, similar groups will be formed having the average factors 80 and 127, while the intermediate spaces will be cleared, the ultimate atoms which occupied these spaces being attracted to the chlorine, bromine, and iodine groupings. These groupings represent what we call elements, but Crookes conjectures that they may possibly consist of an element and a certain number of meta-elements, or that they may each be formed of a whole group of meta-elements, none of which clearly preponderates over the remainder.

One final analogy may help to make the matter clearer. If we suppose that the grouping of our chemical matter is to some extent analogous to the grouping of the heavenly bodies, we should draw a parallel between what we call elements and what we call fixed stars, while meta-elements would correspond to the nebulæ. Just as in a nebula we can have nuclei which will eventually become condensation points for the formation of fixed stars, so in the meta-elements we find kernels which

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resemble ordinary chemical elements to a certain extent, yet which do not show the clean-cut distinctions which we are accustomed to imagine existing between elements. Thus the rare earth group of elements may be regarded as an ill-defined cluster of meta-elements which resemble each other in character, but which for some reason have not coalesced to form a real element.

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CHAPTER XI

THE INACTIVE GASES

1. Historical [1]

In 1893 the Periodic Table of the elements remained very much in the form which it had taken under the hand of Mendeléeff a quarter of a century earlier. Here and there a new element had been discovered, and had taken its place in one of the gaps of the original table; eka-boron (scandium), eka-aluminium (gallium), and eka-silicon (germanium), whose general properties were forecast by Mendeléeff, had been isolated and found to correspond closely to the descriptions which had been theoretically deduced from their position in the Periodic System. But the Table of 1893 contained exactly the same number of spaces as that of 1869, and no one could then have foreseen that in less than half a decade five new elements would be discovered, whose recognition would necessitate the addition to the Periodic System of a new column, and whose properties would be so strange as to differentiate them entirely from any class of elements hitherto isolated. The first of these was argon.

It appears that argon had actually been isolated over a century before it was recognized as a new element. Cavendish, in the course of his researches, had passed electric sparks through air, and, by means of alkalis, had absorbed the oxides of nitrogen thus formed. In this way he obtained as a residue a small bubble of gas which appeared to be unaltered by further sparking. The quantity of substance which Cavendish obtained was too small to allow him to make any experiments

[1] The material for this section was derived from Sir William Ramsay's lecture, "*Die edlen und die radioaktiven Gase*" (1908). See also Ramsay, *The Gases of the Atmosphere;* Travers, *The Study of Gases;* and Ramsay and Travers, "Argon and its Companions," *Phil. Trans.*, 1901, 197 A., 47.

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with it; and when we remember that, even to produce this small amount, it had been necessary for him and his assistant to spend three weeks in turning the handle of a frictional electrical machine, it is not to be wondered that the experiment was not repeated on a larger scale. Cavendish's experiment passed out of the recollection of the majority of chemists, and it was only after argon had been isolated that any attention was paid to it.

In the year 1894 Lord Rayleigh was engaged in an examination of the densities of various elementary gases, and in the course of this work he had occasion to measure the density of nitrogen obtained from two sources. In the one case, he took air and extracted from it carbon dioxide and other impurities, then removed the oxygen, leaving behind atmospheric nitrogen. His other samples of nitrogen were produced from nitric acid or from ammonia. When he came to weigh a litre of the nitrogen prepared in these two ways, he found that instead of getting identical results he appeared to have bodies of different densities, as the following figures show :—

1 litre of atmospheric nitrogen weighed 1·2571 grms.
„ chemically prepared nitrogen weighed 1·2507 grms.

Atmospheric nitrogen was thus 0·0064 gramme per litre heavier than nitrogen derived from pure chemicals.

Rayleigh was inclined to believe that his results could best be explained on the assumption that nitrogen existed in two allotropic forms; so that in the one case he had the ordinary diatomic molecule, while in the other the molecule contained a higher number of atoms. The two gases would then differ from each other as oxygen differs from ozone.

Ramsay, on the other hand, attributed the higher density of the atmospheric nitrogen to the presence in the weighed portion of some hitherto unknown heavier element. To settle the question, experiments were carried out by the two investigators, each working according to a different method.

In the course of one of his lecture experiments before his class, Ramsay had observed that when magnesium is burned in a limited supply of air it combines with nitrogen; for he found that the solid which was left behind after the conclusion of

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the experiment had a strong odour of ammonia. He decided that this property of magnesium would serve the purpose in view; and accordingly he and Williams began a series of experiments, in which atmospheric nitrogen was passed and repassed across heated magnesium. The gas was weighed between each set of experiments, and it was found that its density gradually increased as more and more nitrogen was absorbed by the magnesium. When it passed 16, it became clear that definite results had been obtained, for oxygen was the only possible known impurity. The density of the residue, however, still continued to increase as the gas was passed more and more frequently across the magnesium; it rose to 17·5, when all doubt as to the existence of a new gas was excluded; finally it rose to 19, and there remained constant.

By this process no less than about 100 c.c. of the new gas was obtained; and an examination of its spectrum showed that hitherto unknown lines in the green and red were present in it.

In the mean time Rayleigh had been at work independently, and, by employing Cavendish's method with modern apparatus, had produced about a quarter of a cubic centimetre of the same gas. By diffusion experiments, he proved that the new gas was present in greatest quantity in the less diffusible portions of air, so that it evidently was a comparatively dense substance.

It now remained to ascertain whether the new gas was an element or a compound. Ramsay determined the ratio of the specific heats of the gas at constant pressure and constant volume, finding 1·66 as a result. This coincides with the corresponding value for a monatomic gas, such as mercury. Obviously, then, the new gas was monatomic. But if it were monatomic it must be elementary, as we cannot have a monatomic compound. In this way it was shown that a new element had been discovered.

The fact that the new element did not combine with either magnesium or oxygen had been proved in the course of its isolation, and it was thus made clear that it was chemically very inert. In view of this, its discoverers proposed to name it argon (from *ἀνέργον*, actionless).

About this time, Hillebrand had been engaged in analyzing

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various minerals, and had noticed that those which contained uranium, when they were dissolved in acid, gave off a gas which had a spectrum slightly different from that of nitrogen. Not being thoroughly certain of his spectroscopic results, Hillebrand, in his publications, described the gas simply as nitrogen. Ramsay, being naturally on the look-out for any peculiar sources of nitrogen in nature, procured some of the mineral in question—cleveite—and on boiling with sulphuric acid it was found to yield a gas. Ramsay proceeded to compare the spectrum of this gas with that of argon, and found that in the spectrum of the cleveite gas there was a brilliant yellow line, which he attributed to sodium. Close comparison, however, showed that the yellow line of sodium and that of the cleveite gas did not exactly correspond when they were brought into the field of a comparison spectroscope. Ramsay was at first inclined to believe that the instrument was at fault, and, in order to satisfy himself on the point, took his spectroscope to pieces and rebuilt it. Still the two lines could not be brought into correspondence, and he was driven to the conclusion that he was dealing with a second new gas.

An investigation of the properties of the cleveite gas was then made, and it was found that its density was only twice that of hydrogen, so that the gas was the second lightest in existence. It was discovered that the spectrum of the gas was already known, having been observed in the chromosphere of the sun during a total eclipse. The gas from cleveite, therefore, was identical with the substance previously known to exist in the sun (and hence termed helium), though previous to Ramsay's work it had been supposed that it was confined to the sun, and non-existent on the earth.

An examination of the properties of helium and argon showed that they belonged to the same class of elements. Both were monatomic gases, both were inert as far as chemical properties were concerned. Neither of them could be fitted into the old Periodic Table. Obviously, then, the Periodic System must be modified, in order to find a place for these new elements. A new column was therefore inserted in the table, and helium was placed alongside lithium, while argon fell into position to the left of potassium.

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He	Li	Be
4	7	9
—	Na	Mg
(20)	23	24
A	K	Ca
40	39	40

But this left a gap between argon and helium, which should have been occupied by some element with an atomic weight of about twenty. Ramsay and Travers began an examination of all sorts of natural sources, with a view to finding this element if it existed. They examined seven meteorites, a score of mineral waters, and about a hundred and fifty minerals, but without success. They also recovered the nitrogen from the magnesium nitride which had been formed in the preparation of argon, in the hope that along with it they might be able to detect traces of another gas. Here, also, they were unsuccessful.

About this time liquid air emerged from the stage of being a curiosity, and became obtainable in practical quantities. Ramsay and his assistants evaporated a small quantity of liquid air; took the fraction which was last to evaporate; and, after freeing it from nitrogen and oxygen in the usual manner, they examined its spectrum, and found two new bright lines, one in the green, the other in the yellow, which were hitherto unknown. The density of the gas was investigated, and found to be 22·5. It was therefore higher than that of argon (20), which showed that yet another new gas had been detected. This substance was krypton (κρυπτὸς, hidden).

Fractional distillation of crude liquid argon resulted in the discovery of still another new element, neon.

Since the neon which had been obtained was mixed with helium, it now became necessary to use liquid hydrogen instead of liquid air in the fractionation process. At that time liquid hydrogen had been obtained by Olszewski, but merely traces of it had resulted from his experiments. It had been produced in quantity by Dewar, but he had retained the secret of his process of manufacturing it, so that his method was not available. Ramsay and his collaborators were thus thrown upon their own resources in the matter.

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Travers and Holding therefore devised and constructed, in the laboratory at University College, London, a new machine based upon the Hampson principle, and upon its first trial a few months later this apparatus produced no less than 80 c.c. of liquid hydrogen. A mixture of impure neon and helium from the air was now passed into a flask cooled with this liquid hydrogen, and it was found that the helium remained unliquefied, while the neon became solid. The helium was pumped off, and the solidified neon was gradually warmed. An examination of its density when purified showed that it had an atomic weight of twenty, agreeing with the previous results. The left-hand portion of the Periodic Table then appeared as follows:—

He	Li	Be
4	7	9
Ne	Na	Mg
20	23	24
A	K	Ca
40	39	40
Kr	Rb	Sr
82	85	87
(—)	Cs	Ba
	123	137
**	—	***

The next set of experiments was carried out upon residues of liquid air which had been obtained in the course of attempts to separate neon from argon by the older process. A long series of fractionations resulted in the separation of krypton from argon, argon being pumped off from the krypton. When the krypton was allowed to become warm, after all the argon had been removed, it was observed that some bubbles of gas, apparently not krypton, still remained in the flask. These were collected, and on examination it was found that their spectrum was new. In this way the element xenon was discovered. This substance has an atomic weight of 128, and therefore fits into the above table at the point marked (—).

At that time the elements occupying the positions marked

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with the double and treble asterisk were not known; we shall deal with them in a later chapter.

2. Helium

It has already been mentioned that the helium spectrum had been observed long before the element had been isolated by Ramsay. In the total solar eclipse of August 18, 1868, several astronomers noticed that the spectrum of the solar protuberances contained a brilliant yellow line which lies near the D line of sodium. Lockyer[1] attributed this new line to a new element which he termed helium. In 1882, Palmieri[2] noticed the same line in the spectra of some eruption products of Vesuvius.

Helium is found in nature, though in very small quantity, in some minerals such as bröggerite, fergusonite, cleveite, and meteoric iron; it has been detected also in the waters of certain mineral springs, some of which contain quite a high percentage of the gas. It is also present, though in very small quantities, in the atmosphere.

It is a colourless, tasteless gas, very slightly soluble in water, alcohol, or benzene. It is the least refracting of all gases. The weight of a normal litre of helium is given by Watson[3] as 1·1782 grammes.

Up to 1908 helium resisted all attempts to liquefy it, but in that year Onnes[4] was successful in his attempt, and liquid helium was obtained. It is a colourless liquid with a very slight capillarity, density 0·154, boiling-point 4·5° absolute; the relation between its specific gravity and vapour density is 11·1, so that the critical temperature is not over 5° absolute, and the critical pressure not much above 2·3 atmospheres. Solid helium has not yet been produced.

No compounds of helium are known. Cooke[5] investigated the vapour-densities of various elements in helium and argon

[1] Lockyer, *Proc. Roy. Soc.*, 1868, **16**, 91.
[2] Palmieri, *R. Accad. Napoli*, 1882, **20**, 283.
[3] Watson, *Trans.*, 1910, **97**, 832; see also Ramsay and Collie, *Proc. Roy. Soc.*, 1896, **60**, 206; Ramsay and Travers, *ibid.*, 1897, **62**, 316.
[4] Onnes, *Compt. rend.*, 1908, **147**, 421.
[5] Cooke, *Proc. Roy. Soc.*, 1906, **77**, A., 148.

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at temperatures ranging from 1200° to 1300° C., with a view to finding whether normal or abnormal values were thus obtained. As a comparison, the vapour densities of the same series of elements were determined in hydrogen and nitrogen. Zinc, cadmium, mercury, sulphur, selenium, and arsenic were thus examined, and it was found that the density of cadmium in helium is much higher than in hydrogen, which may point to the formation of a compound of helium with cadmium.

Collie[1] has observed a most peculiar phenomenon in the spectrum of helium when it is mixed with mercury vapour. If we take a tube containing helium under two to five millimetres pressure, and bring into it some mercury vapour, we shall find that the helium spectrum becomes greatly simplified, some of its lines disappearing, while others become fainter. On the other hand, one of the mercury lines which is usually absent from the spectrum of mercury in vacuum tubes appears here very strongly. This line does not make its appearance in tubes filled with hydrogen, argon, or krypton. If the vacuum tube containing helium has a capillary portion with a bore of four millimetres, it is found that only one of the helium lines (green, 4922) appears in addition to the mercury ones.

3. Neon

The method of preparing neon has already been mentioned in the first section of the present chapter, so we need not again go into details with regard to it. The element is a colourless, odourless gas, a normal litre of which weighs 0·9002 ± 0·0003 gramme.[2] Its spectrum is of a peculiar tinge between rose and orange, and this is very brilliant. Like the other gases of this group, neon forms no compounds with other elements.

The most useful property of neon is its power of luminescence under the influence of Hertz waves. If we take a highly exhausted tube of neon and place it across two metallic conductors along which we pass a series of Hertz waves, we shall be able to detect the positions of nodes and loops in the waves by simply running the neon tube along the conductors. When

[1] Collie, *Proc. Roy. Soc.*, 1902, 71, 25.
[2] Watson, *Trans.*, 1910, 97, 832.

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it reaches a loop the tube glows brilliantly, almost as if it were being excited by an induction coil; while at the nodes of the electric vibrations it remains dark. Of course other gases, such as carbon dioxide, will behave in a similar manner; but neon is much more sensitive than any other gas.

Collie has made a curious observation with tubes containing neon. If we evacuate a glass tube containing some mercury, and then fill it with neon, either at atmospheric pressure or below it, we shall find, after sealing the tube, that if we run the mercury up and down the inclined tube the neon will glow just as if a faint Hertz wave were being passed across it. If for a glass tube we substitute a silica one, we can boil the mercury (if the neon's pressure be sufficiently low), and in this case we get a beautiful greenish-white illumination extending through the upper portion of the tube.

4. Argon

The atmosphere contains about one per cent. of argon, which can be extracted from it in the way we have already described in the first section of this chapter. The gas is also found in the waters of many mineral springs.

Like the other elements of this group which we have described, argon is a colourless, odourless, and tasteless gas. Its density is 19·96. A normal litre of argon weighs 1·7809 grammes;[1] the solubility of the gas in water lies between those of oxygen and nitrogen. The argon spectrum is red-orange in colour, duller than that of neon.

At a temperature of −186·1° C., argon is a liquid which yields a solid of melting-point −187·9° C. The solid is a clear mass, which on further cooling becomes opaque.[2] According to Crommelin[3] the critical pressure of argon is 47·996 atmospheres and the critical temperature is −122·44°.

Chemically, argon is inert. Troost and Ouvrard[4] state that

[1] Watson, *Trans.*, 1910, **97**, 836.

[2] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, **64**, 185; **67**, 329; Olszewski, *Phil. Trans.*, 1895, **186**, I., 233.

[3] Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 54.

[4] Troost and Ouvrard, *Compt. rend.*, 1895, **121**, 394.

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they have succeeded in combining it with magnesium vapour; but neither its discoverers nor Moissan [1] were able to form a compound of argon with any other element, even fluorine failing to attack it when the two gases were sparked together. Cooke [2] observed that the vapour density of zinc is higher in argon than in nitrogen, which possibly points to the formation of a compound between the argon and the zinc.

5. Krypton and Xenon

Very little indeed is known beyond the physical properties of these bodies. Both are colourless and odourless gases. The spectrum of krypton is a pale violet, while that of xenon is sky-blue. Both gases have been liquefied, krypton boiling at 121·3° Abs., and xenon at 163·9° Abs, under 760 mm. The weight of a normal litre in the case of krypton is 3·708 grammes, and in the case of xenon 5·851 grammes.[3] No compounds of these elements have been prepared.

The amounts of these two gases which Ramsay and Travers [4] obtained at the time of their discovery were very small: about 22 c.c. of krypton and 3 c.c. of xenon were isolated. Later, Ramsay [5] from 191·1 kilogrammes of air extracted 0·87 c.c. of xenon. This showed that if any gases of higher atomic weight than xenon were present in the atmosphere (presumably in still smaller quantities than the other rare gases), their detection would necessitate the examination of very large quantities of air. Moore [6] has fractionated the residues of no less than a hundred and twenty tons of liquid air furnished by the "Société Air Liquide," but he has obtained no trace of any gas other than those already known. Since, by the methods which he employed, it would have been possible to detect at least 0·03 c.c. of any new gas, it follows that in the hundred tons of air used there cannot have been more than one part in 2,560,000,000 by volume of an unknown gas, should such a body exist at all.

[1] Moissan, *Compt. rend.*, 1895, **120**, 966.
[2] Cooke, *Proc. Roy. Soc.*, 1906, **77** A., 148.
[3] Watson, *Trans.*, 1910, **97**, 836.
[4] Ramsay and Travers, *Phil. Trans.*, 1901, **197** A., 47.
[5] Ramsay, *Proc. Roy. Soc.*, 1903, **71**, 421.
[6] Moore, *Proc. Roy. Soc.*, 1908, **81** A., 195.

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CHAPTER XII

THE RADIOACTIVE ELEMENTS

1. Historical

Within the present generation, we have seen two movements in chemical science which are almost unparalleled in the previous history of the subject. The first of these movements culminated in the decade commencing with 1887. In this year the modern theory of solutions was founded by Arrhenius and van't Hoff, and from this basis the science of physical chemistry began to rise with almost unexampled rapidity. The *Zeitschrift für physikalische Chemie*, first published in 1887, very soon found companions in English and French, and a period of feverish activity in physico-chemical research was opened. To some extent, this wave appears to have spent its force. At the present day, physical chemistry, except in the hands of a few exceptional researchers, has degenerated into a means of attacking the problems of pure chemistry instead of opening up new fields; and consequently there is a certain tendency to decry the subject as a mere means to an end, and not a living branch of science. This is, perhaps, an exaggerated view; but it cannot be denied that physical chemists of the present day are not animated by the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject.* It is, therefore, an extremely fortunate coincidence that as the first movement declined, a second and perhaps more powerful

* Against this it is only fair to quote the views of Bancroft (*J. Physical Chem.*, 1910, **14**, 485). "While there is some truth in this criticism, it is due to the fact that many physical chemists are still interested only in 'the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject.' The difficulty is that most people are still struggling under the limitations imposed deliberately and consciously by Ostwald. Once these are broken through, nobody will have any cause to complain of the wave having spent its force."

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one has succeeded it. This second movement rose with even greater rapidity than pure physical chemistry, and yet at the present day we appear to have touched only the fringe of the subject of radioactivity; so that we may look forward to a long career of fruitful investigation still before us in this department of chemistry. We must now trace briefly the history of the earlier days of this branch.

In 1895, Röntgen showed that when cathode rays impinged upon the end of a vacuum tube they gave rise to a green luminescent patch, from which was projected a series of rays—the X-rays. From the phosphorescence of the Crookes tube to the green phosphorescence of certain minerals is only a short step, and in 1896 Becquerel began an investigation of the latter phenomenon. He found that crystals of potassium uranium sulphate had the property of affecting a sensitive photographic plate (wrapped in black paper) in exactly the same way as it would have been affected by an X-ray discharge. The experiment led to the discovery of what are now called the Becquerel rays.

These radiations are invisible to the eye, just as the X-rays are. They are given off by metallic uranium, and also by uranium salts. Like the X-rays, they can pass through thin sheets of glass or metal; and a further resemblance is to be found in the fact that neither set of rays can be refracted. Again, the Röntgen rays have the property of ionizing gases through which they are passed; and it has been found that in this instance also, the Becquerel rays resemble the others, though their action is much more feeble. If we charge the leaves of a well-insulated electroscope they will remain separated for a very considerable time, owing to the fact that ordinary dry air is a poor conductor of electricity; but if we bring a piece of uranium near the electroscope, the Becquerel rays which are given off from the metal at once ionize the air, making it a better conductor of electricity, and thus the leaves of the electroscope fall together much more rapidly than they did before the uranium was brought near them. We thus have a method of determining the activity of any particular sample of uranium; for we need only measure the rapidity with which an electroscope is discharged when the sample is placed in its vicinity. If the uranium is sending out many Becquerel rays, the electroscope leaves will soon fall together;

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if the Becquerel rays are few, the instrument will be very slowly discharged.

It would naturally be concluded, from the above evidence, that the Becquerel rays and the Röntgen rays were identical. As a matter of fact, however, they are not so. We need not go into details here, as the matter will be dealt with in the next chapter.

Soon after Becquerel's work on uranium and its salts, Schmidt discovered that thorium also had radioactive properties; and since that time various other elements have been described which belong to the same class. Of these the most important is radium.

We need not continue the history of the subject further in this section. The present chapter will be devoted to a discussion of the various radioactive metals. In the following chapter, some account will be given of the changes which these bodies spontaneously undergo. The final chapter of the volume will contain a description of the gases which are evolved during radioactive change. Of course, in the space at our disposal, no attempt can be made to treat the subject in great detail. The properties of radium and its derivatives will be taken as typical and described at some length, while the allied substances will be dealt with very briefly.

2. Radium

In this and the succeeding sections we shall attempt to give an outline of the properties of the various radioactive substances. To enter fully into the physical side of the question would carry us beyond the limits of the present volume; so, as far as possible, the subject will be treated from the point of view of chemistry, and the physical part of the subject will be dealt with only in so far as it aids the comprehension of the purely chemical side.

In the introductory section of this chapter, attention was called to the fact that uranium salts throw off radiations which affect photographic plates just as the X-rays do. Now, uranium compounds are found naturally in the mineral pitchblende, which occurs usually (like the rare earths) in igneous rocks such as

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granite. Madame Curie,[1] in the course of an examination of a great number of naturally occurring substances, discovered that in some cases the natural ore was much more radioactive than the amount of uranium salt contained in it would lead us to expect. For example, pitchblendes are about four times as active as metallic uranium; chalcolite (a double phosphate of uranium and copper) is twice as active as uranium. Further, when Madame Curie prepared artificial chalcolite, she found that instead of being more active than metallic uranium, it was two and a half times less active. This proves conclusively that the activity of the natural chalcolite was not due entirely to the uranium contained in it, but must be attributed to the presence in the natural ore of some substance not found in the synthetic product.

Having thus established the presence of a new body in pitchblende and other minerals, the question of extraction then arose. It was easy to carry out an ordinary analysis, and to determine by measurements with an electroscope whether the activity was a property of the filtrate or of the precipitate. We need not enter into any details with regard to the method of analysis employed. The opposite table gives a rough idea of the series of operations which must be gone through before we can obtain a mixture consisting of radium chloride with barium chloride.

Having in this way obtained a mixture of the bromides of radium and barium, it is necessary to separate them from each other. This is done by fractional crystallization, either from aqueous solution or from a solution of the salts in water acidified with hydrobromic acid. The latter is the better method of the two. It is possible to employ the method of fractional precipitation instead of crystallization, the mixed salts being thrown down from an aqueous solution by means of alcohol. In either case, the radium bromide is less soluble than the barium salt.

The radium salts which are obtained in this way resemble the corresponding barium compounds in many respects. Radium chloride is isomorphous with barium chloride, and the

[1] Thesis presented to the Faculté des Sciences, Paris; see *Chem. News*, 1903, **88**, 85, 97, 134, 145, 159, 169, 175, 187, 199, 211, 223, 235, 247, 259, 271.

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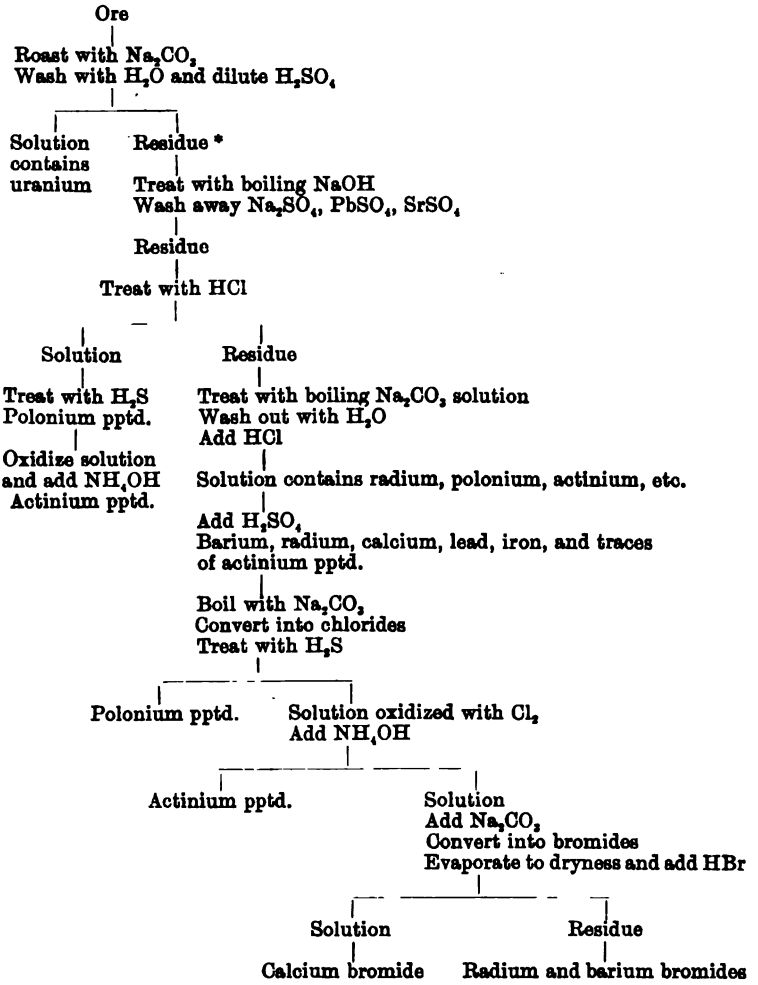

two salts, when they are freshly prepared, are similar to each other in appearance. It has been found that if we allow the radium salt to stand for a time it gradually becomes coloured, the tint ranging from yellow to rose-pink. The coloration becomes much more marked if a trace of impurity (such as a barium salt) be present in the crystals.

* This residue contains sulphates of radium, lead, and calcium, silica, alumina and iron oxide, together with traces of many other metals.

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Another property which is noticeably altered by lapse of time is the blue luminescence exhibited by freshly prepared radium salts or their solutions. The presence of barium salts in this case also appears to have some influence, for the blue light is more strongly exhibited by an impure sample of radium salt than it is by a pure one.

An aqueous solution of a radium salt has been found to evolve a mixture of oxygen and hydrogen, and there appears to be no cessation of this process, which offers such a peculiar parallel to electrolytic action.[1] A still more extraordinary property of these salts, however, remains to be described. Curie and Laborde[2] observed that the temperature of a radium salt appears to be always a little higher than the temperature of the air about it; in other words, the radium salts are continually giving out heat. Curie and Laborde made some investigations of this phenomenon, and showed that the quantity of heat disengaged in one hour by one gramme of pure radium would amount to about a hundred gramme calories.

When a radium salt is placed in the flame of a Bunsen burner it gives rise to an intense carmine-red coloration, which is very characteristic. The spectrum of the element has been examined by several workers, and found to be quite different from any known spectrum; which lends weight to the assumption that radium is an element and not a compound, as some authors have suggested.

The atomic weight of radium has been the cause of considerable controversy. Madame Curie,[3] in the course of her researches, determined this constant by estimating the chlorine in a sample of radium chloride. A control experiment with the same quantity of barium chloride yielded reasonably accurate results, so there seems no ground for supposing that the radium determination was erroneous owing to too small a quantity of material being used. The value for the atomic weight of radium obtained in this way was 225. Runge and Precht,[4] from considerations of the spectra of radium salts under the influence of magnetic fields, came to the conclusion

[1] See also Ramsay, *Monatsh.*, 1908, **29**, 1013.
[2] Curie and Laborde, *Compt. rend.*, 1903, **136**, 673.
[3] Madame Curie, *Chem. News*, 1903, **88**, 159.
[4] Runge and Precht, *Physik. Zeitsch.*, 1903, **4**, 285.

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that this value was much too low, and instead of it they proposed the number 258. Watts,[1] also from measurements of spectra, concluded that Madame Curie's value was much more likely to be accurate than was that of Runge and Precht. This seems to be justified; for the Runge and Precht results would imply that Madame Curie had not less than twenty-five per cent. of bárium chloride in her "pure" radium salt, which is hardly credible. Madame Curie[2] has recently repeated her determination of the atomic weight, using no less than 0·4 gramme of radium chloride, and her second result agrees very closely with that which she originally obtained. The mean of three consecutive concordant results is 226·2, where silver is taken as 107·8 and chlorine as 35·4. It seems probable that this value is near the mark. Thorpe,[3] in 1908, obtained three results (226·8, 225·7, 227·7), whose mean is 226·7. If we accept this value for the atomic weight of radium, we find that it places the metal in the column of the Periodic Table which contains the alkaline earths, radium falling under barium. This position of the new element is quite in accordance with the general chemical character of its salts, which resemble those of barium so closely.

There is another set of properties which the radium salts show, but since these are dependent upon the Becquerel rays rather than upon the radium salts themselves, we shall postpone the consideration of them until the following chapter.

Metallic radium has recently been isolated by Madame Curie and Debierne.[4] A solution containing about a decigramme of radium chloride was electrolysed, the cathode being mercury and the anode being platinum-iridium. After the electrolysis was completed, the amalgam of radium at the cathode was placed in an iron boat and heated in a current of hydrogen which had previously been purified by passage through the walls of a platinum tube heated in an electric furnace. At approximately 700° C., the mercury had all been driven off and the boat contained a brilliant white metal which fused sharply in the neighbourhood of 700° C. and began to attack the quartz

[1] Watts, *Phil. Mag.*, (6) 1908, **6**, 64.
[2] Madame Curie, *Compt. rend.*, 1907, **145**, 422.
[3] Thorpe, *Proc. Roy. Soc.*, 1908, **80**, 298.
[4] Madame Curie and Debierne, *Compt. rend.*, 1910, **151**, 523.

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tube in which the experiment was carried out. On exposure to air, a black film formed upon the metal, this being probably radium nitride. Radium attacks water violently, forming a soluble oxide. A trace of the metal having fallen upon a sheet of paper, it was found that the paper was blackened and apparently carbonised. It appears that metallic radium is more volatile than barium.

3. Polonium

A glance at the table on p. 207 will recall the fact that at one point in the preparation of radium we get a solution which, on treatment with sulphuretted hydrogen, yields a precipitate of polonium. The precipitate of course contains other metallic sulphides, such as those of bismuth, copper, and lead. Madame Curie did not succeed in separating polonium from the bismuth with which it is mixed; but Marckwald [1] has devised a method by means of which the polonium may be isolated and concentrated very simply. If we add some stannous chloride to a solution containing polonium, tellurium, etc., the whole of the active substance is precipitated in the form of a fine precipitate. Now, if to a solution containing tellurium as an impurity we add first hydrazine hydrochloride, we shall precipitate all the tellurium, leaving the active substance in solution. The addition of stannous chloride to this solution will now precipitate the active substance. Polonium may also be obtained by immersing in its solution a plate of metallic bismuth; the polonium is deposited on the bismuth surface, leaving the solution inactive. This method of separation, however, does not seem to be of much practical value.

It appears that polonium is closely allied to tellurium; and it has been shown by Rutherford [2] that it is almost certainly one of the decomposition products of radium, radium F, with which we shall deal more fully in the last chapter of this volume.

A considerable quantity of polonium has recently been

[1] Marckwald, *Ber.*, 1902, **35**, 2285, 4239; 1903, **36**, 2662.
[2] Rutherford, *Phil. Mag.*, (6) 1905, **10**, 300.

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obtained by Madame Curie and Debierne[1] and its spectrum has been investigated; but the research is not yet complete.

Though no definite measurements have been made, there is evidence which makes it probable that polonium is an element with an atomic weight of about 210, and that it lies in the column of the Periodic Table just below tellurium.

4. Actinium

Recurring to the table on p. 207, it will be noticed that the substance actinium is precipitated along with metals of the iron group. It was discovered by Debierne[2] in uranium residues, but up to the present time has not been obtained in a pure state. It appears to be identical with Giesel's emanium.[3] In the impure condition, the actinium salts are very much more radioactive than the thorium salts with which they occur in nature. Actinium appears to lie between calcium and lanthanum as far as its purely chemical properties are concerned.[4]

The separation of actinium salts from those of thorium and the rare earths is a very tedious process, and is usually carried out by means of a solution containing an actinium compound along with some other salt which can be cleanly precipitated. The precipitation of the second substance traps the active body, which is thus brought down in the precipitate. For example, if we take a solution of actinium and barium salts and precipitate the barium in the form of sulphate, we shall find that the precipitate is radioactive owing to the presence in it of actinium sulphate. Instead of barium salts, we may use the precipitation of neutral nitrate solutions by means of oxygenated water, or the action of sodium thiosulphate upon slightly acidified salt solutions. In both these cases the active body is brought down in the precipitate. If we precipitate the rare earth elements as hydroxides, suspend these in water, and

[1] Madame Curie and Debierne, *Compt. rend.*, 1910, **50**, 386.

[2] Debierne, *Compt. rend.*, 1899, **129**, 593; 1900, **130**, 206; 1903, **136**, 446, 767; 1904, **139**, 538; 1905, **141**, 383.

[3] Giesel, *Ber.*, 1902, **35**, 3608; 1903, **36**, 342; 1904, **37**, 1696, 3963; 1905, **38**, 775; 1907, **40**, 3011; *Physikal. Zeitsch.*, 1904, **5**, 822.

[4] Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, 119, [iia] 1.

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add hydrofluoric acid, we shall find that the major part of the active substance remains unattacked and does not pass into solution. A recent research of Welsbach's[1] has shown that in presence of ammonium salts actinium is not completely precipitated either by ammonia or by ammonium oxalate, but that from basic solutions, in presence of manganese, it is precipitated as a manganate.

5. Uranium

In the first section of this chapter we mentioned some of the properties of uranium salts the investigation of which led to the discovery of the radioactive phenomena. Uranium in itself is of very little importance from the present point of view, and we shall reserve a discussion of its properties for the following chapter, in which we shall consider its relations to radium and the other radioactive substances. These relations are brought out in the course of some changes which the radioactive substances undergo on standing, and they throw a little light upon the problem of the origin of radium. We need only state in this place that the properties of uranium itself resemble more or less closely those of radium.

6. Thorium

The question of the radioactivity of thorium is one of the most contested of all. Originally it was supposed that the radioactivity shown by thorium compounds was due to the activity of the thorium atom, but various authors have adduced evidence to the contrary. Hofmann and Strauss,[2] in the preparation of thorium from bröggerite, cleveite, and samarskite, obtained active products. It was observed later by Hofmann and Zerban[3] that these thorium preparations did not retain their activity permanently, but that the radioactive power of the substances gradually decayed. This pointed to the view that the activity of the thorium was not similar to that of radium, but belonged to the class of phenomena termed "induced

[1] Welsbach, *Sitsber. K. Akad. Wiss. Wien*, 1910, 119 [iia] 1.
[2] Hofmann and Strauss, *Ber.*, 1909, **33**, 3126.
[3] Hofmann and Zerban, *Ber.*, 1902, **35**, 531; 1903, **36**, 3093.

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activity," with which we shall deal later in this volume. Induced activity is produced by bringing a non-active body into the presence of an active one, from which proximity it derives a transitory activity. Induced activity persists for a time even after the inducing body is removed.

Now, Hofmann and Zerban showed that along with the thorium in the minerals investigated by them there was always present a certain amount of uranium, and to this they ascribed the presence of the activity. Further, the more rich in uranium the ore was, the more radioactive was the thorium extracted from it. Finally, they procured some Brazilian monazite sand which contained no uranium, and found that the thorium extracted from it was inactive, but if it were heated to 400° C. with active uranium oxide it acquired activity.

Against this we must set the investigations of Barker,[1] who examined photographically the activity of thorium from uranium-free monazite sand obtained in Brazil and North Carolina. In every case activity was detected, in spite of the absence of uranium from the mineral.

Zerban[2] then carried out a series of analyses of various monazite sands from various parts of the world, and found that in every case uranium was present when the thorium was active.

Baskerville and Zerban,[3] in 1904, discovered inactive thorium in a South American mineral, consisting for the most part of barium carbonate. Neither the barium nor the thorium in the mineral showed a trace of activity. Zerban[4] contradicts this.

In 1905 further light was thrown upon the problem by the work of Ramsay and Hahn,[5] who discovered that when a mixture of radium and barium bromides obtained from about five thousand pounds of thorianite was fractionated, the activity of the soluble part did not diminish regularly as was expected, but became greater after a series of fractional crystallizations. When ammonia was added to these solutions, a precipitate was obtained which had very active properties. Further research

[1] Barker, *Amer. J. Sci.* (4), 1903, **16**, 161.
[2] Zerban, *Ber.*, 1903, **36**, 3911.
[3] Baskerville and Zerban, *J. Amer. Chem. Soc.*, 1904, **26**, 1642.
[4] Zerban, *Ber.*, 1905, **38**, 557.
[5] See Hahn, *Zeitsch. physikal Chem.*, 1905, **51**, 717.

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in conjunction with Sackur showed Hahn that he had obtained a new radioactive body which is very closely related to thorium.

The chief difficulty encountered in the isolation of radiothorium is due to the fact that it is very difficult to separate it from radium. The method employed is as follows. The separation of the radium from radiothorium is carried out by means of a series of precipitations of iron salts in the radium-radiothorium solution. In this way the radiothorium is entangled in the iron precipitate, and separated from the radium salt. The removal of the iron salt is then accomplished in either of several ways. We may add ammonium carbonate in the cold, filter, and then boil; or we may convert the salts into sulphates, acidify, and precipitate with a little ammonia. In this way the radiothorium is thrown down before the iron. Again, we may take a solution of the oxalate, make it slightly acid, and then just neutralize it. In this way we produce a slight flocky, strongly active precipitate, which is insoluble in excess of ammonium oxalate.

Elster and Geitel[1] have discovered the same substance in the thermal springs of Baden-Baden.

Recent research has shown that the thorium problem is even more complicated. Hahn's investigations[2] led him to the conclusion that between thorium and radiothorium a third substance must be interposed, to which the name mesothorium has been given. Further work[3] suggests that this intermediate body is made up of two parts, which have been named thorium-1 and thorium-2. On this nomenclature, radiothorium would be called thorium-3.

The chief practical interest of the mixture known as mesothorium lies in the fact that its chemical and radioactive properties are very closely allied to those of radium itself; so that adulteration of radium preparations with mesothorium might lead to considerable inconvenience, the more so since mesothorium is by comparison a very short-lived substance. It is possible to detect the admixture of the mesothorium by measurements of the intensity of the penetrating rays given off

[1] Elster and Geitel, *Physik. Zeitsch.*, 1906, **7**, 445.
[2] Hahn, *Ber.*, 1907, **40**, 1462.
[3] Hahn, *Physikal. Zeitsch.*, 1908, **9**, 255.

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by the adulterated preparation at intervals of a month. The suspected preparation is freed from emanation and its activity observed. After three weeks, more emanation should have accumulated and the radioactivity can be calculated from the first result. If the second result does not agree with this, then it is clear that pure radium salts are not present.

7. Lead

As in the case of thorium, a considerable controversy has centred about the question of the radioactivity of lead. In 1899, Elster and Geitel[1] discovered that lead sulphate derived from pitchblende had radioactive properties; but since they were able to produce inactive lead sulphate by chemical means, they concluded that the activity of the other samples must have been due to the presence in it of some radium or other active element, and was not ascribable to the activity of the lead itself. Giesel[2] in his researches also encountered this radioactive form of lead, but was not convinced that it was actually radioactive *per se*. Hofmann and his co-workers[3] believed that they actually had radioactive lead in their possession, and that it differed to some extent in chemical properties from ordinary lead; but Giesel,[4] who was supplied with some of their material, was unable to detect the differences which they described.

Boltwood and Rutherford[5] have come to the conclusion that radio-lead is really one of the decomposition products of radium, radium D, with whose constants the figures obtained by Hofmann and his collaborators are in close agreement.

8. Ionium

This body was discovered by Boltwood,[6] who at first mistook it for actinium. The uranium ore carnotite is the source from

[1] Elster and Geitel, *Annalen der Physik*, 1899, **69**, 83.

[2] Giesel, *Ber.*, 1900, **33**, 3569; 1901, **34**, 3772; 1902, **35**, 102.

[3] Hofmann and Strauss, *Ber.*, 1901, **34**, 3083, 3970; Hofmann and Wölfl, *Ber.*, 1902, **35**, 692, 1453; 1903, **36**, 1040; Hofmann, Gonder, and Wölfl, *Annalen der Physik*, 1904, **15**, 615.

[4] Giesel, *Ber.*, 1901, **34**, 3772.

[5] Boltwood, *Phil. Mag.*, [6] 1905, **9**, 599; Rutherford, *ibid.*, 1905, **10**, 290.

[6] Boltwood, *Amer. J. Sci.*, (4) **25**, 365; see also Welsbach, *Sitzsungsber. K. Akad. Wiss. Wien*, 1910, **119** [iia], 1.

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which the element has been obtained, and the mode of preparation is as follows. The ore is dissolved in hydrochloric acid, chlorides of the rare earths are then added to the solution, and the whole is precipitated in the form of oxalates. Further purification is carried out by repeated precipitation with thiosulphates. Very little is known with regard to the properties of ionium. It appears to be very closely related to thorium. As will be seen in the next chapter, there is evidence tending to prove that ionium is the parent substance whose degradation produces radium, while ionium itself appears to be a decomposition product of uranium.

9. Potassium and Rubidium

The numerous investigations [1] which have been made of the radioactive properties of potassium seem to show that this element possesses distinct activity. Rubidium also appears to have radioactive powers.

[1] McLennan and Kennedy, *Phil. Mag.*, 1908 (vi.), **16**, 877; Levin and Ruer, *Physikal. Zeitsch.*, 1908, **9**, 248; Strong, *Physical Review*, 1909, **29**, 170; Henriot, *Compt. rend.*, 1909, **148**, 910; Henriot and Vavon, *ibid.*, **149**, 30; Büchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 154; Campbell, *Proc. Camb. Phil. Soc.*, 1909, **15**, 11; Ebler, *Chem. Zeit.*, 1908, **32**, 812.

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CHAPTER XIII

RADIOACTIVE CHANGES

1. The Becquerel Rays

In the previous chapter we mentioned that the salts of radium and other radioactive elements emitted a series of radiations which have been termed the Becquerel rays, from the name of their discoverer. Since a very considerable part of the peculiar activity of radioactive bodies is closely connected with these rays, it is necessary at this point to enter into some consideration of the question. The first problem which we have to solve is that of the nature of the rays in question. Are they simple, or are they made up of a series of different types of vibration, such as a mixture of light and X-rays?

To settle this point, we have two methods at our disposal. In the first place, we may interpose in the path of the rays some sort of filter which will give us a chance of separating one component from the rest; or, secondly, we may pass the rays through a magnetic field, and determine whether they are uniformly deflected as a whole or whether they can be resolved into a series of vibrations having different deflections.

We need not enter into any great detail with regard to the first of these methods. An experiment mentioned by Strutt[1] will make the application clear. Suppose that we charge an electroscope so that the leaves of it diverge from one another. If we now bring near the electroscope a small quantity of a radium salt, we shall find that the leaves fall together, say, in ten seconds. Let us next wrap the radium salt in a sheet of tin-foil and again place it in position near the electroscope; we shall find that the leaves take longer to fall, say, a hundred seconds. We have thus filtered off some part of the rays. Now, if all the rays were of the same type, we should expect to

[1] Strutt, *The Becquerel Rays and the Properties of Radium*, 1904, p. 51.

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increase the time of discharge to a thousand seconds by doubling the sheet of tin-foil. This, however, is not found to be the case; but, instead, the rate of discharge hardly falls at all with the superposition of the second thickness of tin-foil. It is thus made clear that we have filtered off one set of rays by means of the tin-foil, but that there still remain other rays which the tin-foil sheets do not arrest. We have in this way established the presence of two types of vibration, one set stopped by tin-foil, the second not. We have now to discover whether or not we can further sift the rays to which tin-foil is transparent. To do this, we substitute for the tin-foil a thin casing of lead; and here we find a similar behaviour. The addition of one sheet of lead causes a perceptible lengthening of the period of the electroscope's discharge; but the interposition of a second slip of lead does not further diminish the velocity of the discharge to any marked extent. Thus again we have reached a border-line between two sets of rays, one of which will pass through the lead, while the other cannot do so.

This method, however, is only a very rough one, and does not lend itself to measurements of such great accuracy as are obtainable by the second method, in which a magnetic field is used. The actual details of the experimental methods employed need not be described in this place,[1] but we may give the results which have been obtained by the application of the electro-magnet to the problem.

Suppose that we have a magnetic field applied at right angles to the plane of the paper and directed towards the paper; the state of affairs may be represented by Fig. 24.[2]

Here L is a piece of lead in which a hollow has been drilled. At the bottom of the hollow is placed some radium salt, R. Under the influence of the magnetic field, the radiations from the radium salt are split up into three groups, which have been termed by Rutherford the α-, β-, and γ-rays. The γ-rays are not deflected by the magnetic field, and are thus comparable to ordinary X-rays; but their penetrating power is very much greater than that of the X-rays. The β-rays resemble the cathode rays of a high vacuum tube; and like these they are deflected by the magnetic field in the manner shown in the

[1] See Rutherford, *Radioactivity*, 1905, chaps. iv. and v.

[2] Madame Curie, *Chem. News*, 1903, **88**, 169.

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figure. They appear to be streams of particles carrying a negative electric charge. If we place a sensitive photographic plate, PP, under the leaden cell containing the radium salt, we shall find that the spots where the β-rays fall are affected by them. Finally, we come to the third set of components of the Becquerel rays. These, the α-rays, are deflected from the straight path of the discharge by the electric field; but instead of being bent in the same way as the β-rays, they are curved in

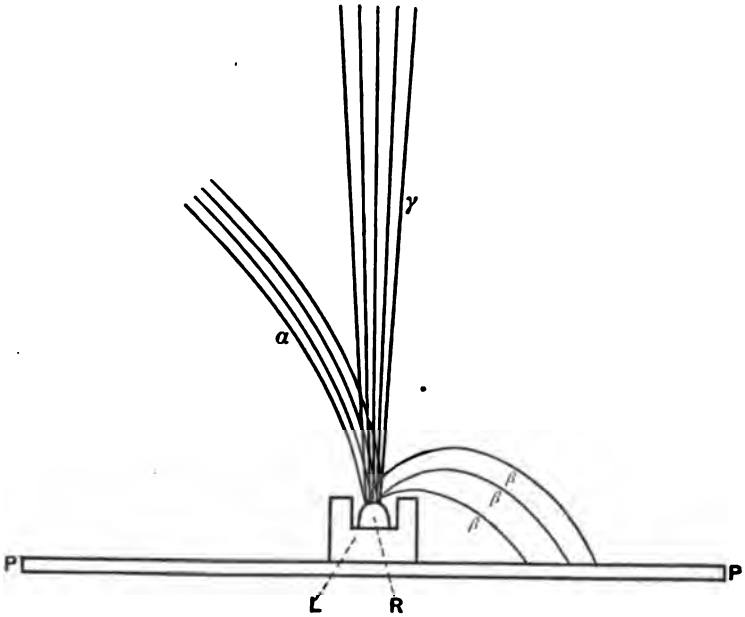

FIG. 24.

the opposite direction. They are therefore positively charged particles, and Rutherford supposes them to be helium atoms. We must now discuss the properties of these different rays in turn.

The γ-rays, as we have mentioned, are not deflected to any extent by a magnetic field, even when this is very powerful. Their penetrating power also is very marked. For instance, Strutt[1] has observed that even eight centimetres of sheet lead will not suffice to arrest these radiations. The nature of the

[1] Strutt, *The Becquerel Rays*, p. 83.

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γ-rays seems to be still unsettled. The view[1] that they are streams of particles has been controverted[2] on the ground of their showing no deflection in the magnetic field. The other view of their nature supposes them to resemble the X-rays. Now, the X-rays may be conjectured to be non-periodic pulses in the ether which are set up when electrons are suddenly stopped in their paths by some obstacle. This view explains the production of these vibrations at the point where the cathode rays of a high vacuum tube strike the glass of the tube. Applying this idea to the case of radium, and bearing in mind the fact that the β-rays of radium and the cathode rays of a Crookes tube are very closely allied, we might come to the conclusion that the γ-rays of radium salts were produced by the bombardment of the solid salt by the particles of the β-rays produced within itself. Another view[3] of the γ-rays assumes that they are made up of discrete particles discharged at very high velocity, each particle being a "neutral-pair" composed of one negative and one positive electron. This hypothesis, as far as it concerns the γ-rays, appears to agree with the known data, but its application to the problem of the nature of X-rays, which closely resemble the γ-rays, appears to be contested.

The nature of the β-rays seems to be now beyond doubt. They are material particles projected from the surface of the radium salt, just as particles are driven out from the cathode of a high vacuum tube. Naturally, they do not all travel with the same velocity; some sets of particles move more slowly than others, and it has been found possible to analyze the swarm of particles by deflecting them in magnetic fields. It has been found that the slowest-moving particles are most deflected—as can be foreseen—and it has been proved, further, that the β-rays as a whole are less deflected than the cathode rays from Crookes tubes. Hence it is clear that the particles forming the β-rays of radium are moving at a much higher velocity than those which are shot out by the cathodes of vacuum tubes. It has been estimated that the velocities of

[1] Paschen, *Annalen d. Physik*, 1904, **14**, 114, 889; *Physikal. Zeitsch.*, 1904, **5**, 568.

[2] Rutherford, *Radioactivity*, 1905, pp. 182 ff.

[3] Bragg, *Phil. Mag.*, 1907, [vi.], **14**, 429.

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light, the β-rays, and the ordinary cathode rays are approximately the following:—

Light . . .	30×10^4	kilometres per second
β-rays . . .	(6×10^4) to (28×10^4)	,, ,, ,,
Cathode rays .	(2×10^4) to (10×10^4)	,, ,, ,,

It appears, then, that the velocity of the electrons in the β-rays is greater than that of any other known natural body. From the fact that the radioactive bodies are losing negative electricity at a considerable rate owing to the departure of the electrons of the β-rays, it is clear that the remaining portion of the salt must gradually acquire a positive charge, and that if loss of this charge be prevented by insulation it will eventually become quite measurable. In point of fact, one experimenter[1] noticed that when a sealed glass tube containing radium was opened after several months, a bright electric spark was produced.

Turning now to the α-rays, we enter quite a different field. Here we have to deal with what appears to be a series of heavy particles, such as helium atoms, travelling at high velocities (probably one-tenth that of light). These bodies are positively charged, and are deflected by magnetic fields in the direction opposite to that taken by the β-particles. The extent of the deflection, however, is by no means so great as that observed in the case of the electrons of the β-rays. The α-rays appear to be very similar in character to the canal-rays which can be produced in vacuum tubes. It seems certain that the heat generated by radium is due to the impacts of these particles. Crookes has devised an instrument, the spinthariscope, by means of which we can actually observe the effects of the collision between α-particles and ordinary matter. The spinthariscope consists of a zinc sulphide screen, above which a tiny fragment of a radioactive substance is suspended on the end of a steel pointer. When the screen is examined through a lens, it is found to be covered with tiny points of light which appear and vanish almost at once. These light-spots are due to the phenomenon known as triboluminescence, in which the breaking of a crystal causes a flash of light; and it is supposed that the flashes in the spinthariscope are caused by the fracture of the zinc sulphide crystals under the impact of helium atoms discharged from the radioactive substance on the pointer. The

[1] Dorn, *Physikal. Zeitsch.*, 1903, **4**, 507.

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triboluminescence phenomena on a larger scale can be observed by any one who rubs two pieces of sugar together in the dark.

In the foregoing paragraphs we have discussed the properties of the α-, β-, and γ-rays *seriatim;* but we must bear in mind that the effects produced by radium in general are not caused by the separate action of each type or ray, but are really due to the united action of all three kinds. We shall now give a few instances of the changes which radium produces upon various substances when it is placed in their vicinity.

The first effects which are recognizable are those due to fluorescence or luminescence of one kind or another. Suppose that we bring an X-ray fluorescent screen near a radium compound; the screen will become strongly lit up, just as it is when acted upon by the Röntgen rays. Bary[1] has found that many of the alkali metals and alkaline earths are also fluorescent when brought into the neighbourhood of a radium preparation. Madame Curie[2] showed that paper, cotton, and other substances could exhibit the same phenomenon. Becquerel[3] observed that while a ruby will fluoresce under the action of light-rays, it remains inert with regard to radium. Again, a diamond which shines in presence of the rays from radium does not light up when X-rays are thrown upon it; and calcium sulphide appears to behave similarly. Many other instances of this action of the Becquerel rays might be quoted.

If we expose a fluorescent substance of the type mentioned above to the continued action of the radium rays, it is found that the power of shining which it possesses does not remain constant, but slowly diminishes, while at the same time the physical appearance of the fluorescent body changes. Barium platinocyanide on long exposure to the rays grows darker in colour, finally becoming quite brown; its luminescence also dies away gradually. Both the original colour and the power of fluorescing can be regenerated by exposing the salt to light for a time.

When some varieties of glass are exposed to the action of the Becquerel rays they become fluorescent, and at the same time become tinted brown or violet according to the alkali metal

[1] Bary, *Compt. rend.*, 1900, **130**, 776.
[2] Madame Curie, *Chem. News*, 1903, **88**, 212.
[3] Becquerel, *Compt. rend.*, 1899, **129**, 912.

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contained in them. If we warm the glass after the process has gone on for a time, we shall find that it loses its tint and becomes again transparent, regaining at the same time its original power of fluorescence. Not only so, but when heated it now possesses the power of spontaneous fluorescence. The same is true for such minerals as fluorspar.

Owing to the presence of the γ-rays in the Becquerel rays, the latter have the power of ionizing gases, just as the X-rays do. We need not enter into details with regard to this property; it is obvious that the electroscopic method of determining activity depends upon it.

In many cases the action of the Becquerel rays upon ordinary chemical elements or compounds is well marked. For instance, the Curies have shown that by their influence we can convert oxygen into ozone.[1] Again, if we submit yellow phosphorus to the action of the radiations, it becomes changed into the red allotropic modification.[2] On the other hand, it has been shown by Sudborough [3] that the presence of radium salts has no influence upon some geometrically isomeric substances which are transmuted into the stable form by the action of light. If we allow the Becquerel rays to act upon a solution of iodoform in chloroform, we shall find that it becomes purple owing to the separation of iodine.[4]

The physiological effects of the radium radiations are very striking. If a radium salt be allowed to remain in contact with the skin for even a few minutes, it is apt to produce extremely painful eruptions; and these are the more troublesome owing to the fact that they take a considerable time to make their appearance. Thus even by bringing radium near the skin, without actual contact, we may produce very deep-seated changes in the tissues without having any outward sign that we have injured them. The action of the radiations upon the tissues is apparently due to the breakdown of lecithine, which makes up a considerable part of the epidermis. This destructive character of the radium salts, however, is not without its uses, for in cases of rodent ulcer it has been successfully employed to cure the

[1] *Compt. rend.*, 1899, **129**, 823.
[2] Becquerel, *Compt. rend.*, 1901, **133**, 709.
[3] Sudborough, *Proc.*, 1904, **20**, 166.
[4] Hardy and Willcock, *Proc. Roy. Soc.*, 1903, **72**, 200.

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disease; and at the present time we seem to be on the verge of considerable advances in this direction. Hardy[1] has found that the coagulation of globulin may be brought about by the influence of the Becquerel rays, and in this case the action appears to be due to the positive charge carried by the α-particles.

2. The Disintegration Hypothesis[2]

When we consider that the radium salts form what appears to be an inexhaustible store of energy, we are naturally driven to inquire from what source this energy is derived. In reply to this question, two main hypotheses must be considered. In the first place, we may imagine that the radium salts are mere energy-transformers which catch up some external force from their surroundings and convert it into the Becquerel rays in some manner which we do not as yet understand; or, secondly, we may suppose that the source of the energy is to be sought in the radium atom itself. The first view pictures radium as a sort of dynamo which can convert, say, heat into X-rays; the second hypothesis regards it rather as a kind of chemical compound like diazo-benzene, which is so unstable that it may spontaneously decompose with a great outburst of energy. It will be seen that the first of these ideas is a physical one, while the second is chemical. At the present time the chemical explanation appears to have gained the day, and we must now describe some of the phenomena upon which it is based.

Crookes,[3] in the course of an investigation of the properties of uranium, found that if a uranium salt were precipitated by means of ammonium carbonate and the precipitate treated with excess of the reagent, the precipitate almost entirely redissolved, leaving behind it only a very slight residue. The redissolved uranium was found to be radioactively inert, while all the original radioactivity appeared to be concentrated in the small residue. The residue Crookes termed uranium X. So far, there was nothing out of the common; it appeared that the

[1] Hardy, *Proc. Physiol. Soc.*, 1903, XXIX.

[2] See Rutherford, *Radioactivity;* Rutherford and Soddy, *Phil. Mag.*, (6), 1903, **5**, 576.

[3] Crookes, *Proc. Roy. Soc.*, 1900, **66**, 409.

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activity of uranium was really due to the presence in it of this trace of uranium X. A much more important result was obtained later, however, when it was found that the inactive uranium, after standing for some months, became once more radioactive.*

About the same time, Becquerel [1] separated uranium and uranium X in another way. He mixed solutions of uranium and barium salts, and then, on precipitating the barium as sulphate, he found that the barium had acquired radioactive properties, while the uranium had lost them. After standing for a year, the two products were re-examined, and it was found that by that time the barium had lost its activity, while the uranium was again as radioactive as it was at the beginning of the experiments.

The only possible conclusion which can be drawn from these results is that the activity of uranium is due to some substance which is produced spontaneously by uranium.

Rutherford and Soddy [2] found a similar series of phenomena in the case of thorium, and they proceeded to investigate quantitatively the rate at which thorium X lost its activity. They found that, starting with inactive thorium and active thorium X, after four days the thorium had regained half its original activity, while in the same time the thorium X had lost half its radioactive powers. The rate of decay and recovery can be expressed in both cases by exponential equations :—

$$\text{For the decay of Th X,} \qquad I_t = I_0 \times e^{-\lambda t}$$

$$\text{For recovery of Th activity,} \quad I_t = I_0(1 - e^{-\lambda t})$$

in which I_0 represents the initial activity of the thorium or the thorium X, I_t the activity after a time t has elapsed, and e the base of the Napierian logarithms. The factor λ, it is found, is the same for both decay and recovery. Similar results were obtained with uranium and uranium X, except that in this case the period during which the uranium X lost half its activity was about twenty-two days, instead of four as in the case of thorium.

* The activity determinations were made photographically, and are thus concerned only with the β-rays; had the α-rays been used as a test, the uranium would not have appeared to lose much activity.

[1] Becquerel, *Compt. rend.*, 1900, **131**, 137; 1901, **133**, 977.

[2] Rutherford and Soddy, *Trans.*, 1901, **81**, 321, 837.

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The most striking peculiarity of this decay and regeneration is the fact that it is totally unaffected by changes of temperature, even a white heat appearing to have no accelerating influence. This differentiates it from the ordinary chemical reactions, which are all more or less susceptible to changes of temperature.

There is one other point which we must mention. It has been shown that the degree of activity of any salt is directly proportional to the amount of the radioactive element in the salt, and has no connection with the acidic part of the molecule. The activity of radium bromide is different from that of radium carbonate, and depends purely, in each case, upon the percentage of radium metal in the salt.

From the foregoing evidence, we can draw certain conclusions. In the first place, the fact that the percentage of radioactive element present in a salt is the measure of its activity proves conclusively that radioactivity is a property of the atom, and not of the molecule. Secondly, the fact that radioactive change is independent of temperature proves that we are not dealing with an ordinary molecular decomposition. We must therefore have to do with some new atomic property. Finally, since the α-particles which are driven out in the Becquerel rays are material bodies, we are obviously witnessing the breakdown of some material system; and from what has gone before it is obvious that this system cannot be a molecular one. It must therefore be intra-atomic.

We cannot go into further details with regard to the evidence upon which the disintegration hypothesis is based, but must now proceed to describe briefly the outlines of the hypothesis itself.

Rutherford,[1] taking the case of thorium as an example, sets forth his views as follows. The thorium atoms are supposed to be semi-stable systems of which some break down every second. The number of collapsing systems is relatively small when compared with the total number of thorium atoms present in any specimen; Rutherford estimates that about one atom in every 10^{16} will suffice. When the atom of thorium becomes unstable, it disintegrates and expels from the system one or more α-particles. The remaining particles rearrange themselves into

[1] Rutherford, *Radioactivity*, pp. 286–7.

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a new semi-stable system. For simplicity's sake let us suppose that each thorium atom expels one α-particle. The α-particles of thorium resemble those of radium very closely; and since the radium particles have twice the mass of a hydrogen atom, it is probable that those of thorium have approximately this mass. These α-particles constitute what is termed the "*non-separable activity*" of thorium, which amounts to about 25 per cent. of the maximum. Now, the new semi-stable system, thorium X, formed after the expulsion of the first α-particle from the thorium atom,* is much less stable than thorium itself. In turn, it throws off an α-particle. These second α-particles give rise to the "*radiation*" from thorium X. Since the radioactivity of thorium X falls to half its value in four days, it is clear that on the average half the atoms of thorium X must disintegrate in four days, the number decomposing per second being always proportional to the number of atoms present. Now, as we shall see in the next chapter, thorium X in turn undergoes a whole series of changes, giving rise successively to thorium emanation and a set of other active bodies. We may represent these changes diagramatically thus—

$$\begin{array}{ccccc} \alpha\text{-Particle} & & \alpha\text{-Particle} & & \alpha\text{-Particle} \\ \uparrow & & \uparrow & & \uparrow \\ \text{THORIUM} & \rightarrow & \text{THORIUM X} & \rightarrow & \text{THORIUM EMANATION} \rightarrow \end{array}$$

The disintegration of the thorium atom, on this hypothesis, gives rise to a series of substances, each of which will differ in chemical properties from its predecessors.

The following table[1] will give a general idea of the disintegration products which are formed in the decomposition of the radioactive elements. In the second column is given the value of the constant λ of the exponential equation which we have

* This is Rutherford's original statement. Recent work by Hahn (*Physikal. Zeitsch.*, 1908, **9**, 245) has shown that there are products intermediate between thorium and thorium X, the complete series being represented by—

$$\text{Thorium } (\alpha\text{-rays}) \rightarrow \underbrace{\text{Thorium-1 (rayless)} \rightarrow \text{Thorium-2 } (\beta\text{-rays})}_{\text{Meso-thorium}} \rightarrow \underbrace{\text{Thorium-3 } (\alpha\text{-rays})}_{\text{Radio-thorium}} \rightarrow \text{Thorium X}$$

[1] Rutherford, *Radioactivity*, p. 449; Ramsay, *Trans.*, 1909, **95**, 627, with modifications.

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THORIUM, ACTINIUM, AND THEIR DEGRADATION PRODUCTS.

Products.	$\lambda(sec)^{-1}$	T	Nature of rays.	Properties of products.
Thorium . .	—	—	α	Insoluble in NH_4OH.
↓ Thorium-1 .	—	5·5 years	No rays	—
↓ Thorium-2 .	—	6·2 hours	β	—
↓ Thorium-3 .	—	2 years	α	—
↓ Thorium X .	2×10^{-6}	4 days	α	Soluble in NH_4OH and water.
↓ Emanation .	$1{\cdot}3 \times 10^{-2}$	53 seconds	α	Chemically inert gas of high mol. wt.; condenses at − 120° C.
↓ Thorium A .	$1{\cdot}74 \times 10^{-3}$	11 hours	No rays	Deposited on bodies; concentrated on cathode in an electric field; soluble in some acids; Th A more volatile than Th B; shows definite electrochemical behaviour.
↓ Thorium B .	$2{\cdot}2 \times 10^{-4}$	55 minutes	α, β, γ	
↓ ? . .	—	—	—	—
Actinium. .	—	—	No rays	Insoluble in NH_4OH.
↑ Actinium X .	$7{\cdot}8 \times 10^{-7}$	10·2 days	α (? β)	Soluble in NH_4OH.
↓ Emanation .	0·17	3·9 seconds	α	Behaves like a gas.
↓ Actinium A .	$3{\cdot}2 \times 10^{-4}$	36 minutes	No rays	Deposited on bodies; concentrated on cathode; soluble in NH_4 and strong acids; volatilized at about 100° C.; A and B can be separated by electrolysis.
↓ Actinium B .	$5{\cdot}4 \times 10^{-3}$	2·15 minutes	α, β, γ	
↓ ? . .	—	—	—	—

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URANIUM, RADIUM, AND THEIR DEGRADATION PRODUCTS.

Products.		$\lambda(\text{sec})^{-1}$	T	Nature of rays.	Properties of products.
Uranium		—	—	α	Soluble in excess $(NH_4)_2CO_3$; soluble in ether.
↓					
Uranium X		$3{\cdot}6 \times 10^{-7}$	22 days	β and γ	Insoluble in excess $(NH_4)_2CO_3$; soluble in ether and water.
↓					
Ionium		—	—	—	—
↓					
Radium		—	1300 years	α	Resembles barium, but more electronegative; halides soluble; sulphate and carbonate sparingly soluble.
↓					
Emanation		$2{\cdot}1 \times 10^{-6}$	3·8 days	α	Chemically inert gas; condenses at low temperature; atomic weight 216?
↓	Active deposit of rapid change				
Radium A		$3{\cdot}85 \times 10^{-3}$	3 minutes	α	Deposited on bodies; concentrates on cathode; soluble in strong acids; volatile at 1000° C.
↓					
Radium B		$5{\cdot}38 \times 10^{-4}$	21 minutes	No rays	Precipitated along with barium; soluble in strong acids; volatile at 630° C.
↓					
Radium C		$4{\cdot}13 \times 10^{-4}$	28 minutes	α, β, γ	Deposits on copper or nickel; soluble in strong acids; volatile at about 1000° C.
↓					
Radium D		—	About 40 years	No rays	Possibly radio-lead; soluble in strong acids; volatile below 1000° C.
↓					
Radium E_1		—	6 to 6·5 days	No rays	Soluble in hot acetic acid; volatile below 1000° C.
↓					
Radium E_2		—	4·8 days	β and γ	More electronegative than E_1; volatile at red heat.
↓					
Radium F		$5{\cdot}6 \times 10^{-8}$	143 days	α	Probably polonium; deposited on bismuth; volatile at 1000° C.
↓					
?		—	—	—	—

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already quoted. T represents the time taken for each radioactive substance to lose half its activity. The third column contains notes on the nature of the radiations emitted by each active body.

We need not enter into a discussion of the various emanations from the radioactive substance, as these gases and their decomposition products will form the subject of the next chapter.

3. The Origin of Radium

From the table given in the previous section, it will be seen that the radioactive elements are continually being transformed into other forms of matter. This has been established by purely experimental evidence, and is independent of any theoretical views as to the mechanism by means of which the transformation is accomplished. Now, if we imagine that we have a gramme of radium at the present day, it is clear that in thirteen centuries half of it will have been converted into emanation; and, since we have no means of reconverting the emanation into radium, this half of the radium has ceased to exist as such. Another thirteen centuries will see our gramme of radium reduced to a quarter of a gramme, and in the end, after the lapse of a few million years, the amount of radium remaining from our original gramme will be non-existent from a practical point of view. Of course, in theory the disintegration will go on for an infinitely long period; but in practice a geologically brief interval of time would be sufficient to reduce any reasonably large quantity of radium to an amount so small as to be beyond our present resources for its detection. Rutherford[1] calculates that in twenty-six thousand years a kilogramme of radium would be reduced to one milligramme of active substance, the rest having disintegrated. Thus, if the whole earth had been made up of radium twenty-six thousand years ago, its activity at the present day would be no greater than that which we observe in pitchblende.

From considerations such as these, we are driven to conclude that the radium which we isolate from pitchblende at the

[1] Rutherford, *Radioactivity*, p. 459.

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present day cannot have been in existence in the early stages of the earth's history. It must, therefore, have come into existence at a more recent date, and we should be able to throw some light upon its origin by a careful investigation of the substances which occur along with it in the natural state.

Rutherford and Soddy [1] put forward the idea that radium itself was a disintegration product whose parent was one of the substances which occur in pitchblende. Now, of these substances two can be at once singled out from the others. Uranium and thorium have all the characteristics which would be required by the hypothetical parent of radium. Both have higher atomic weights than radium, and both decay more slowly than radium does. On examination, it is found, however, that these two bodies do not occur with equal profusion in the radium ores: pitchblendes containing radium are usually rich in uranium, but the thorium ores do not generally contain radium. It therefore appears probable that uranium, rather than thorium, is the parent of radium.

McCoy [2] has shown that the radioactivity of a uranium ore which does not contain any thorium is proportional to the amount of uranium which it contains. This goes to prove, of course, that there is a close relation between the quantity of uranium and the amount of radium or its congeners present in the mineral. Similar results have been obtained by Strutt [3] and Boltwood,[4] who have proved that the ratio of uranium to radium in radium ores is almost constant. Soddy and Mackenzie [5] made some experiments with uranium which had been freed from radium and left to stand for a time. They concluded that some radium was produced.

Boltwood [6] has apparently solved the problem, though the solution is a somewhat unexpected one. Since it had been shown by himself, as well as by Soddy, that the rate of production of radium from uranium was slower than it was expected

[1] Rutherford and Soddy, *Phil. Mag.*, (6) 1903, **5**.

[2] McCoy, *Ber.*, 1904, **37**, 2641.

[3] Strutt, *Proc. Roy. Soc.*, 1905, **76** A., 88.

[4] Boltwood, *Phil. Mag.*, (6) 1905, **9**, 599.

[5] Soddy, *Phil. Mag.*, (6) 1905, **9**, 768; Soddy and Mackenzie, *ibid.*, 1907, **14**, 272. Compare Whetham, *Nature*, 1904, **70**, 5; 1905, **71**, 319.

[6] Boltwood, *Amer. J. Sci.*, (4) 1905, **20**, 239; 1906, **22**, 537; **24**, 370; 1908, **25**, 365.

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to be, Boltwood came to the conclusion that radium was not the direct descendant of uranium, but that instead there was an intermediate step which must be some hitherto unknown element. Boltwood at first imagined that this intermediate element must be actinium, being led to that conclusion by the following results. From carnotite, a mineral which contains about twenty per cent. of uranium, he extracted the actinium it contained by repeatedly precipitating that element as oxalate. After standing for a couple of months, the actinium was once more taken in hand, and all the emanation which it had accumulated was boiled off. After sufficient time had elapsed to allow the actinium emanation to disintegrate (its half life-period is only a few seconds), the emanation was examined and found to correspond in quantity to that which would be liberated from $5{\cdot}7 \times 10^{-9}$ grammes of radium. It was therefore concluded that the actinium solution contained this quantity of radium. On repeating the work a hundred and ninety-three days later, it was found that the amount of radium emanation present corresponded to the presence in the solution of no less than $14{\cdot}2 \times 10^{-9}$ grammes of radium. The only explanation for the presence of the extra $8{\cdot}5 \times 10^{-9}$ grammes of radium appears to be that it is produced from the actinium in the solution.

Rutherford[1] then showed that what Boltwood imagined to be actinium could not be that element, for it could be separated from true actinium by means of ammonium sulphide. (A mixture of ammonium and sodium thiosulphates appears to be a better reagent for this separation.) It appears that the solution of this supposed actinium gives none of the characteristic degradation products of actinium. Boltwood found that the activity of the new body—to which he gave the name ionium—was about seventy-six per cent. of that of radium. Hahn[2] independently came to somewhat similar conclusions, basing these upon the results which he had obtained in the course of some extractions of thorium salts from monazite sand. He observed that the amount of radium in the thorium preparations depended upon the time which had elapsed since their extraction from the sand; and these measurements furnished

[1] Rutherford, *Nature*, **76**, 126.
[2] Hahn, *Ber.*, 1907, **40**, 4415.

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means of calculating the rate of the formation of the radium. The half life-period of radium from Hahn's experiments is about thirteen hundred years, which is in good agreement with Rutherford's theoretical results.

Thus it appears, that, though uranium is an ancestor of radium, it is not the latter's direct parent. The line of descent is apparently from uranium to ionium, and then to radium.

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CHAPTER XIV

RADIOACTIVE EMANATIONS

1. The Emanations from Thorium and Actinium

In 1899 Owens[1] was engaged in an examination of the radiation effects of various thorium derivatives, and in the course of the work he observed that the radiations were by no means constant when measured electrically. Further investigation showed that the inconstancy was due to air-currents about the apparatus; for when the experiments were carried out in closed vessels, the ionization of the air reached a maximum and then remained constant. Now, if radioactive effects can be influenced simply by passing air across the radioactive substance which forms the subject of the experiment, it seems probable that part, at least, of the radioactive influence is due to some material which can be mechanically blown away by the current of air. This material might be either a gas or a cloud of tiny particles of thorium, which had been loosened from the main body of the radioactive mass.

Rutherford[2] pursued this line of research, and was able to prove that thorium did actually liberate something which we may term an emanation, and that this emanation had radioactive properties. He showed that the properties of the emanation very closely approximated to those of a gas. For instance, it can be blown about by gas-currents; it can be bubbled through liquids; a mica stopper will prevent it escaping; and, finally, it causes no deposition of water-globules in the dust-counter. This last experiment proves that the emanation is not a cloud of thorium particles, for these would of course form nuclei for the condensation of water; while the molecules of a gas would be too small to produce this effect.

[1] Owens, *Phil. Mag.*, (6) 1899, **48**, 360.
[2] Rutherford, *Phil. Mag.*, (6) 1900, **49**, 1.

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The activity of the emanation was found to decay very rapidly. To measure this decrease in activity, a very ingenious method was employed, the outline of which is as follows. Pure air was blown across some thorium salt, and in this way became mixed with the emanation from the thorium; the mixed gases were then passed into a long brass cylinder through whose walls projected three insulated electrodes. The brass cylinder was insulated and connected with a battery; and the current through the gas was measured by means of an electrometer in the usual way. It was found that the current diminished progressively along the cylinder; and by passing the stream of mixed gases at different rates through the tube, it was possible to determine the rate of decay of the emanation. Le Rossignol and Gimingham [1] found that the activity of the emanation fell to half value in fifty-one seconds.

In the light of this work, it seemed probable that the other radioactive elements also might give off analogous emanations. Debierne [2] showed that this was true in the case of actinium, which gives off a gas having properties similar to those of thorium emanation, though its time of decay is very much shorter—about four seconds. This substance does not call for detailed treatment, as the general properties of thorium and actinium emanations resemble those of radium emanation, with which we shall now deal in some detail in the next section.

2. Niton *

The discovery of thorium emanation speedily led to that of the emanation from radium, which was detected in 1900 by Dorn.[3] It resembles the thorium derivative in most respects, but is much more durable.

When we consider the amount of emanation which is evolved from a given quantity of radium, the first thing which forces itself upon our notice is the difficulty which would be

[1] Le Rossignol and Gimingham, *Phil. Mag.*, (6) 1904, **8**, 107.

[2] Debierne, *Compt. rend.*, 1903, **136**, 146.

* This name has been proposed by Ramsay and Gray as a convenient substitute for "radium emanation."

[3] Dorn, *Abh. d. Naturforscher Gesellsch. Halle*, 1900.

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experienced in handling the minute quantity of gas which can be obtained. It has been found that the amount of emanation from one gramme of radium in radioactive equilibrium has a volume of about one-tenth of a cubic millimetre.[1] Now, the usual quantity of a radium salt used by experimenters varies from 20 to 60 milligrammes, and it must be remembered that only a part of this salt is radium. From these figures it will be seen that the volume of emanation obtainable at any time will be very minute. Consequently, it is necessary to devise some method by means of which we can transfer these tiny bubbles of gas from one vessel to another. It has been found that this is best accomplished by mixing the emanation with a large quantity of a neutral gas, such as air. The mixed gases can then be transferred from vessel to vessel without any appreciable loss of emanation. One of the simplest ways of obtaining this mixture of emanation and air is to bubble air through a solution of radium bromide in water.

Niton behaves as an ordinary gas. It obeys Boyle's Law,[2] and diffuses like other gases when placed in a vessel. Experiments have been made by various workers,[3] with a view to determine the molecular weight of niton from its rate of diffusion, but the results are, of course, extremely inaccurate. It must be borne in mind that in these diffusion experiments we are dealing with a very minute quantity of niton mixed with a very large volume of some indifferent gas, so that the results are affected by many factors which do not come into view in ordinary diffusion experiments. All that we can safely conclude from these investigations is that the molecular weight of niton, to judge from its density, must be very high, probably over a hundred. As we shall see later, this estimate is under the mark.

Niton has been liquefied and its critical constants have been determined by Ramsay and Gray.[4] The liquid emanation

[1] Gray and Ramsay, *Trans.*, 1909, **95**, 1073.

[2] Ramsay, *Compt. rend.*, 1904, **138**, 1388.

[3] Rutherford and Brooks, *Trans. Roy. Soc. Can.*, (2) 1902, **7**, 21; *Chem. News*, 1902, **85**, 196; Curie and Danne, *Compt. rend.*, 1903, **136**, 1314; Bumstead and Wheeler, *Amer. J. Sci.*, (4) 1904, **17**, 97; Makower, *Phil. Mag.*, (6) 1905, **9**, 56.

[4] Gray and Ramsay, *Trans.*, 1909, **95**, 1073.

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is colourless and transparent by transmitted light. It is phosphorescent and shines with a colour which varies with the nature of the glass of the tube in which it is enclosed, the usual tints being green to lilac. When highly compressed, the tint resembles that of a cyanogen flame, being slightly bluish-pink. The solid emanation is not transparent. It melts at $-71°$ C. Like the liquid, the solid phase of the emanation is phosphorescent; but the colour of the phosphorescence is much more brilliant, and its colour varies with the temperature. On cooling below the melting-point, the tint of the emitted light is steel-blue; further cooling changes it to yellow, and it finally becomes orange-red. On warming the tube containing it, the colours reappear in inverted sequence. The red phosphorescence disappears at $-118°$ C., while at $-59°$ C. or $-60°$ C. the liquid is dull bluish-green. The critical temperature is 377°·5 Abs., and the vapour-pressure at this temperature is 47,450 mm.

The most recent attempt to determine the atomic weight of niton is that carried out by Gray and Ramsay,[1] whose method consisted in weighing a given volume of the gas. When it is remembered that the total volume which they were able to obtain at any one time was less than 0·1 c.mm. some idea of the difficulties of the research will be obtained.

Evidence with which we shall deal later in this chapter proves conclusively that niton belongs to the inactive gas group of elements; and making the usual assumptions with regard to the periodic arrangement of the elements, we can predict that niton will lie somewhere above xenon in the scale. Its atomic weight might therefore be either 176 or 222 approximately, as the following figures show, since the difference between two successive atomic weights in this column is generally about forty-five:—

Hellum.	Neon.	Argon.	Krypton.	Xenon.	I.	II.
4	20	40	88	180	176	222

If the figure 222 were correct, then 0·1 c.mm. of niton would weigh less than 1/1400 milligramme; and in order to weigh this small mass with sufficient accuracy it was necessary to devise a balance which would turn with a load of not more

[1] Gray and Ramsay, *Proc. Roy. Soc.*, 1911, A., 84, 536.

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than a hundred-thousandth of a milligramme. The production of this balance is certainly the high-water mark of modern physico-chemical technique. We cannot enter into details of the construction of this apparatus, but must confine ourselves to a brief description of its essentials. The beam of the balance is formed from threads of quartz fibre, and carries a small mirror of platinized silica. Instead of weights, a counterpoise is used which consists of a small quantity of air sealed up in a quartz bulb. The whole balance is surrounded by an air-tight case in which the pressure can be varied by means of a pump. When the air-pressure in the balance is the same as that in the bulb, the apparent weight of the bulb's contents is nil. In a vacuum, the sealed-up air exerts its full weight, as it is not counterpoised by the buoyancy of the air outside in the case. At any pressure intermediate between ordinary pressure and a vacuum, the apparent weight of the air in the bulb can be calculated. In this way, by varying the pressure of air in the case, we can bring the balance into equipoise; and this can be determined by throwing a beam of light from the platinized mirror on to a scale some feet away from the apparatus. Many corrections are necessary in the course of a weighing, but for an account of these the reader is referred to the original paper. The results obtained by Ramsay and Gray give a mean atomic weight of niton equal to 223; so that niton should lie two places above xenon in the Periodic Table.

The spectrum of niton has been examined by Ramsay and Collie,[1] who have found that it closely resembles in general characteristics the spectra of the inactive gases. The spectrum fades very soon, and is replaced by the hydrogen spectrum. There is one bright line at 5595; Ramsay and Collie suggest that this may be identical with a line in the spectrum of lightning[2] which does not seem to have been identified with that given by any known gas.

Like radium itself, radium emanation spontaneously gives out a very considerable quantity of heat. The maximum value of heat liberated per hour from the emanation generated by one gramme of radium is given by Rutherford[3] as 75 calories;

[1] Ramsay and Collie, *Proc. Roy. Soc.*, 1904, 73, 470.
[2] Pickering, *Astrophys. J.*, 1901, 14, 368.
[3] Rutherford, *Radioactivity*, p. 431.

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this includes the heat emitted by the disintegration products of the emanation. Niton gives out only α-rays.[1]

It has been shown by Curie and Debierne[2] that the amount of emanation evolved by radium is independent of the pressure to which the radium is subjected; and it has been found that changes of temperature also appear to be without influence upon the rate of formation.

We must now turn to the chemical nature of niton. It has been shown by Rutherford and Soddy[3] that the emanations of thorium and of radium both showed an extraordinary inertness even when submitted to the action of strong chemical reagents. For example, no change could be detected in the gas after passing it over red-hot platinum black, or finely divided palladium, lead chromate, magnesium powder, or zinc dust. Such inertness can be paralleled only by the elements of the argon group; and it seems evident that niton must be reckoned as belonging to that class of bodies. Ramsay and Soddy[4] have made even more stringent tests, by sparking niton with oxygen in presence of alkali—a process which brings even nitrogen into combination—as well as by passing a mixture of air and niton over a highly heated mixture of magnesium powder and lime. In the latter case the mixture of gases was passed for three hours across the magnesium-lime mixture which was heated to a bright redness; the measurements of the radioactivity of the niton made before and after the experiment gave exactly the same result. In the course of these experiments it was found, further, that niton is unattacked even by phosphorus burning in oxygen.

From the results quoted in the foregoing paragraphs, we can now assign to niton a place in the Periodic Table. From the chemical evidence, it is clear that niton is one of the inactive gases; and the evidence of its physical constants makes it practically certain that it must lie above xenon in the Table. Thus its position in the table on p. 198 lies below the double asterisk.

If niton *per se* is inert, it displays a very great influence

[1] Rutherford and Soddy, *Phil. Mag.*, (6) 1903, **5**, 445.
[2] Curie and Debierne, *Compt. rend.*, 1901, **133**, 931.
[3] Rutherford and Soddy, *Phil. Mag.*, (6) 1902, **4**, 580; 1903, **6**, 457.
[4] Ramsay and Soddy, *Proc. Roy. Soc.*, 1902, **72**, 204.

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when brought into contact with other substances. This influence has nothing whatever to do with the chemical reactivity of the gas, but is due purely to its radioactive powers. We must now mention one or two experiments which have been carried out in this field.

Giesel [1] noticed that when a solution of radium bromide was allowed to stand, it evolved some gas which investigation showed to be chiefly hydrogen. Ramsay and Soddy [2] found that the gas mixture contained 29 per cent. of oxygen, the rest being hydrogen. The slight excess of hydrogen they ascribed to contact between the gas mixture and the grease of a tap, which would remove some of the oxygen.

Ramsay [3] carried out a further series of experiments upon the action of niton on water, and found that there was a mean excess of 5·51 per cent. of hydrogen over and above the quantity required to form water with the oxygen liberated. When the gases were stored over mercury, the percentage of hydrogen was still greater, owing to some of the oxygen being used up in oxidation of the mercury. When mercury is not present, various causes of the presence of the excess of hydrogen might be suggested. It was shown that the corresponding amount of oxygen was not lost by oxidation of the radium bromide to bromate, nor was there any formation of ozone or hydrogen peroxide; no bromine is liberated from the radium bromide. In all cases care was taken to prevent the gases coming in contact with tap-grease. Ramsay showed, further, that the action of niton is a reversible one; for while, on the one hand, it decomposes water to produce electrolytic gas, it also has the faculty of recombining oxygen and hydrogen to form water again. In later experiments it was found that traces of hydrogen peroxide may be formed by the action of niton upon water.

We shall have to return to this subject in a later section, but enough has been said to show that niton possesses simultaneously two sets of properties which, before its discovery, it would have been hard to believe capable of co-existence. On

[1] Giesel, *Ber.*, 1902, **35**, 3605.

[2] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 294.

[3] Ramsay, *Trans.*, 1907, **91**, 931; Cameron and Ramsay, *ibid.*, 1908, **93**, 966, 992.

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the one hand, it is itself chemically inert; but, on the other hand, it can influence the chemical properties of other substances to a very marked extent. There is one other property which it exhibits, and this is perhaps the most extraordinary of all. Spontaneously it is transformed into another element, helium.

Before dealing with the disintegration of niton, however, it will be well to mention some experiments which throw some light upon the earlier stages of the decompositions which it undergoes. Ramsay and Soddy[1] made an investigation of the volume of the emanation, with a view to determining whether or not the substance remained constant. The results which they obtained are given in the following table:—

Time in days.	Volume in c.c.
Start.	0·124
1	0·027
3	0·011
4	0·0095
6	0·0063
7	0·0050
9	0·0041
11	0·0020
12	0·0011
28	0·0004

The first number seems very large in comparison with the others; this may possibly be due to an uncondensable gas being present and forced into the walls of the tube.

From these results it is clear that the emanation is gradually disappearing. Now, we need not suppose that matter is being destroyed, but rather that something akin to the condensation of a gas to the liquid state is taking place, which will, of course, be accompanied by a contraction in volume. The simplest hypothesis is that the gaseous emanation which was derived from solid radium is undergoing a further change which is reconverting it into a solid substance.

Here we touch another line of evidence tending to prove the same point, and we must turn aside to consider the phenomena which are classed under the heading *excited activity*.

It was shown by M. and Mme. Curie[2] in the case of radium,

[1] Ramsay and Soddy, *Zeitsch. physikal. Chem.*, 1904, **48**, 691.
[2] M. and Mme. Curie, *Compt. rend.*, 1899, **129**, 714.

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and by Rutherford independently [1] in the case of thorium, that these substances have the faculty, when placed near other bodies, of communicating to the latter the power of exhibiting the phenomena of radioactivity. Debierne [2] later found that actinium had a similar property.

We need not describe the experiments which have established the laws governing this phenomenon, but we may summarize the results which have been obtained. It is found that the strength of the excited activity depends, not upon the nature of the object upon which it is located, but purely upon the strength of the activity of the exciting radioactive preparation, and the length of time that it was left in the neighbourhood of the excited object. After the radioactive substance has been removed from the neighbourhood of the excited object, the latter begins to lose its radioactive properties, and the decay of these follows an exponential curve. Further research proved that the excited activity is proportional to the amount of emanation present.

Now, Rutherford [3] has shown that if a platinum wire is exposed to thorium emanation it becomes endued with excited activity. If we immerse a wire so treated in hot water, very little change can be detected in the activity when it is withdrawn and dried; but if we immerse the wire in concentrated hydrochloric acid, we shall find that the activity is lost by the wire, but is acquired by the solution; and, further, if we evaporate the solution to dryness, we shall find that the activity has been transferred to the dish. This active matter can be removed from the wire or the dish by simple scraping.

All this goes to show that we are dealing now with a solid substance, and not with a gas. But if we have a solid substance, it might be supposed to be a compound of the emanation with the platinum of the wire. This view is quite untenable, when we consider that red-hot platinum black will not attack the emanation; so we are driven to conclude that the emanation has deposited the solid substance upon the platinum.

Thus the results of measurements of diminution in the volume of the emanation, as well as those phenomena which we

[1] Rutherford, *Radioactivity*, p. 295.
[2] Debierne, *Compt. rend.*, 1904, **138**, 411.
[3] Rutherford, *Phil. Mag.*, (6) 1900, **49**, 188.

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have just described, point alike to the view that the emanations of radium and thorium are continually being transformed into solid substances.

Further investigation of the rate of decay in the case of excited activity showed that this solid *active deposit* (as Rutherford terms it) was not a permanent substance, but was one which rapidly passed through a series of changes. Instead of the decay being expressible by the usual exponential equation—

$$I_t = I_0 \times e^{-\lambda t}$$

it is found that it really follows the exponential law, but that the total decay series is made up of different factors. The first decay period has one value for λ, the second has another value for λ, and the third yet another. This proves, of course, that the primary radioactive deposit is first converted into a second one, having a different radioactive capacity; and that this second one is in turn changed into a third substance which has a decay constant different from that of its predecessors.

In this way the existence of the radium derivates A, B, C, D, E, and F has been established, and it has been possible to compare them with other bodies by a comparison of the decay constants of the two substances. The chief point of interest in these substances lies in the fact that radium D, E, and F are found in radio-lead, which appears to owe its activity to their presence; while polonium appears to have constants agreeing with those of radium F.

3. The Production of Helium

Though the measurements of radioactive decay mentioned in the last section were sufficient to show that the emanation from radium was capable of undergoing transformation into other forms of matter, the results were not quite convincing, for, to some extent, the proof depended upon certain theoretical assumptions which were incapable of rigid demonstration. The quantities of the transformation products were extremely small; and no chemical or spectroscopic experiments could be made which threw much light upon the differences between the various substances. It was not until Ramsay and Soddy[1]

[1] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 206; 1904, **73**, 346. A

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began their work upon the emanation that a product was actually observed whose chemical individuality was beyond doubt.

Rutherford and Soddy,[1] after finding that niton was an inert gas, put forward the view that it belonged to the argon family; and they further pointed out the fact that helium is always found in minerals which contain uranium or thorium. The question as to whether this association of helium with the radioactive minerals had any connection with their activity was thus opened.

Ramsay and Soddy took 20 milligrammes of radium bromide which had been prepared three months previous to their experiments, dissolved it in water, and collected the gas which was evolved. This gas was for the most part electrolytic gas, which had been produced by the action of the radium and radium emanation upon the water; but it also contained some emanation. To separate the latter from the other gases, the mixture was passed over a red-hot, partly oxidized copper spiral, and the water so formed was removed by means of phosphorus pentoxide. After this the gas was passed into a tiny vacuum tube, in which the spectrum was examined and carbon dioxide detected. This gas was eliminated by means of liquid air, and a re-examination of the spectrum in the small vacuum tube showed the presence of helium, the D_3 line being visible. Further experiments were made, and practically all the lines in the helium spectrum were found. This work has been confirmed by several workers,[2] and it has been shown that actinium also gives rise to helium.[3]

In this way, it was proved conclusively that radium emanation actually gives rise to helium. The objection might be made that the helium is present throughout the course of the experiments; but this is shown to be untenable by the fact that the helium spectrum is not visible at first. When an examination is made at the beginning of the process, it is found that a new spectrum is visible which does not contain the

translation of these papers appeared in *Zeitsch. physikal. Chem.*, 1904, **47**, 490; **48**, 682.

[1] Rutherford and Soddy, *Phil. Mag.*, (6) 1902, **4**, 581.

[2] Dewar and Curie, *Compt. rend.*, 1904, **138**, 190; Meyer and Himstedt, *Ann. d. Physik.*, 1904, **15**, 184.

[3] Debierne, *Compt. rend.*, 1905, **141**, 383; Giesel, *Ber.*, 1907, **40**, 3011.

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helium lines; the latter develop slowly and are visible only some days after the emanation has been brought into the vacuum tube. For instance, in one experiment the emanation was led into the vacuum tube on July 17; the new spectrum—probably that of the emanation—was then observed, which contained no helium lines. After standing until the 21st, the helium spectrum was observed, and compared with that of a helium vacuum tube.

It is thus shown that the helium is not present in the earlier part of the experiments, nor is it in any way connected with the presence of the radium salt in the solution; it is derived from the emanation alone. In this way the disintegration hypothesis has obtained its strongest support. Previous to the work of Ramsay and Soddy, the evidence in favour of this hypothesis depended, to a great extent, upon postulates which could not be experimentally tested; but by the production of helium from the emanation, the breakdown of one radioactive substance into a non-active body was conclusively demonstrated.

These experiments throw light upon another point. It has been found that helium exists in many minerals, as well as in the waters of several mineral springs; and for a considerable time the presence of this very rare gas under such conditions was inexplicable. Ramsay and Soddy's researches have cleared up this question also; for it has been shown that both minerals and mineral waters which contain helium have also more or less well-marked radioactive properties. They are therefore certain to contain a small proportion of radioactive emanation, and it is doubtless from this source that helium is derived.

4. Transmutation

It has already been mentioned that either radium or radium emanation, when brought into contact with water, decomposes the latter just as an electric current does. Apparently this action is confined to the liquid state, for steam does not appear to be affected in the same manner.[1] Hydrochloric acid is broken down into hydrogen and chlorine under the same circumstances. This parallel between the actions of the emanation and the

[1] Cameron and Ramsay, *Trans.*, 1908, **93**, 966.

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electric current led Ramsay [1] to try the effect of the emanation upon a solution of copper sulphate, from which, by analogy, he expected to get copper deposited and little or no hydrogen evolved. The actual results, however, were much more striking.

Radium emanation, when allowed to break down spontaneously, either alone or in presence of oxygen and hydrogen, yields helium. When the decomposition took place in contact with water, Ramsay observed the presence of neon at the end of the experiment. When copper sulphate was dissolved in the water, *no helium was produced;* but the presence of argon was detected. Further, traces of lithium were found in the copper salt solution after the emanation had acted upon it, though none were detected in the blank experiments carried out at the same time and under the same conditions.

These experiments created a considerable sensation in the chemical world, and the further detailed account of the work was eagerly awaited. This was published shortly afterwards.[2]

The experiments were carried out in the following manner. In the first place, pure laboratory copper sulphate was dissolved in pure water and was electrolyzed. The copper was deposited upon a rotating cathode of smooth platinum. After washing with pure water, about half a gramme of the copper was dissolved in a few c.c. of redistilled nitric acid; the solution was evaporated to dryness on the water-bath, and the solid was heated for a time to expel nitric acid. The nitrate was then dissolved in pure water, and filtered into two glass bulbs newly made from the same piece of tubing. The first was treated with several accumulations of emanation, after which it was sealed off and the emanation was allowed to decay; the other tube was exhausted and sealed off.

In other experiments, the electrolytically deposited copper was dissolved in "contact" sulphuric acid. After the experiment had been completed, this copper was recovered in the form of sulphide, converted into the acetylide, and this in turn into the nitrate, which was used for a further series of experiments.

[1] Ramsay, *Nature*, 1907, **76**, 269.

[2] Cameron and Ramsay, *Trans.*, 1907, **91**, 1593; 1908, **93**, 992; see also Cameron's account of the experiments in *Science Progress*, 1908, **3**, 222.

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After the expiration of sufficient time to allow the emanation to decay, the copper salt solution was transferred to a platinum crucible and saturated with sulphuretted hydrogen, which was passed in through a platinum tube. The precipitated sulphide was separated by centrifuging it in a silica tube. The filtrate was then evaporated to dryness and ignited, after which the residue was treated with a few drops of pure water. This solution was then evaporated and examined spectroscopically. The whole of the analysis was carried out in platinum or silica vessels.

In both experiments calcium and sodium were detected in the residue. Lithium was found in the case of the bulb which had been treated with emanation, but not in the untreated bulb.

We might account for the presence of this lithium in four different ways. In the first place, it may be due to impurity in the copper salts employed; secondly, it might have been ascribed to the action of water or the emanation upon the glass of the bulb; thirdly, it might be introduced in the course of analysis; or, finally, it might be the disintegration product of one of the elements present, just as helium is formed as a disintegration product of the emanation.

The fact that lithium is found only in the sample treated with emanation, but not in the untreated sample, though the two are originally derived from the same solution, appears to negative the idea that the lithium is an impurity of the copper salts used. With regard to the idea that the lithium may be derived from the glass of the bulb, it might be mentioned that some of the experiments were carried out in silica bulbs, and in these cases the same results were obtained. Further, no lithium was observed in cases where glass bulbs were used in blank experiments, either when they contained copper solutions or emanation in contact with water. There seems no possibility of accounting for the presence of lithium being due to error in the analyses; the precautions which were taken are inconsistent with this assumption.

We are therefore driven to conclude that the lithium must be formed in some way from the contents of the bulbs under the action of the radium emanation which they contain.

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We must now turn to the details of the results which were obtained by an analysis of the gases remaining in the bulbs after the experiments. The bulb into which no emanation had been introduced contained, of course, no gas. The bulb which had contained emanation was now filled with a mixture of gases, which was analyzed in the usual way. The results are given below, and as a comparison the figures which are obtained when pure water is treated with emanation in the same manner are given also.

	Copper nitrate solution. c.c.	Pure water. c.c.
NO	1·12	—
N_2	0·34	0·307
CO_2	0·27	0·065
CO	—	0·030
H_2	0·44	8·746
O_2	1·12	1·562

It will be noticed that the greatest difference between the two columns is to be found in the case of the hydrogen evolved in the two cases. In the copper nitrate solution the liberated hydrogen may have been used up in reducing the nitric acid, which would also account for the large amount of nitric oxide produced.

The nitrogen and nitric oxide were removed by the ordinary methods, and the residual gases examined spectroscopically. No helium or neon was observed, but argon was present in quantity. This could not have leaked or diffused in from the outer air, for if this were the case the helium spectrum also should have been observed.

The gaseous residue from the bulb in which pure water had been treated with emanation was then examined, and it was found to show a brilliant neon spectrum, while the helium lines were not pronounced. This proved that the decomposition of the emanation had not followed the usual course; for in that case no less than five cubic millimetres of helium should have been present, whose spectrum would have far outshone that of the neon.

Some objections have been raised in connection with this work. Soddy and Mackenzie[1] state that traces of neon and

[1] Soddy and Mackenzie, *Proc. Roy. Soc.*, 1908, A. 92.

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helium can be obtained from electrodes which have been used in an atmosphere of these gases, or even from fresh aluminium electrodes. This observation, however, hardly seems sufficient to account for the comparatively large quantities of neon detected by Ramsay and Cameron, or for the fact that these authors, using the same spectrum tubes, did not invariably find the neon spectrum. Rutherford and Royds[1] state that they have not been able to detect more than a trace of neon when radium emanation is allowed to act upon water, and they attribute the presence of this trace to a leakage of air. Mme. Curie and Mdlle. Gleditsch[2] have repeated the Ramsay and Cameron experiments, using platinum vessels instead of silica or glass ones. Under these circumstances they detected no lithium. Against this we must set the fact that in the Ramsay and Cameron experiments a copper solution divided into two parts showed the presence of lithium in the half which was treated with emanation, while the other half, under precisely similar circumstances except for the presence of the emanation, showed not a trace of lithium; and that this is not an isolated case, but has been observed on several occasions.

In his Presidential Address to the Chemical Society in 1909,[3] Ramsay gave some details of his further experiments, in which he dealt with the products of some salt solutions. From the fact that both radium and actinium yield helium as a disintegration product, Ramsay was led to investigate the behaviour of thorium, with a view to discovering whether it also broke down to the same gas. Two hundred and seventy grammes of thorium nitrate were carefully purified and placed in a round-bottomed flask with a capillary neck, which was then evacuated at intervals until the last traces of gas were removed from it. Precautions were taken to prevent leakage either in or out; and after 168 days the contents were examined. It was found that a certain amount of gas had been collected. This was analyzed, and the experiment repeated twice more, being allowed to stand for 250 days in the one case, and 173 days in the second. The analyses of the gases obtained in these

[1] Rutherford and Royds, *Phil. Mag.*, (6) 1908, **16**, 812.

[2] Curie and Gleditsch, *Compt. rend.*, 1908, **147**, 345.

[3] Ramsay, *Trans.*, 1909, **95**, 624; Ramsay and Usher, *Ber.*, 1909, **42**, 2980.

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three experiments are given below, the figures representing cubic centimetres:—

	Gas volume.	$(H_2 + O_2)$	CO_2	N_2
After 168 days . .	3·523	0·061	—	—
„ 250 „ . .	5·750	0·017	0·588	5·145
„ 173 „ . .	2·74	0·02	1·08	1·64

In each case the gas was examined spectroscopically, but though the D_3 line was detected in more than one case, the results are not sufficient to prove the production of helium from thorium.

On August 14, 1907, a control experiment was started, in which a solution of 300 grammes of mercuric nitrate was used as a blank, being enclosed in a similar flask and dealt with in an identical manner. On March 30, 1908, the gas in the two bulbs gave the following results on analysis:—

Mercury bulb.	Thorium bulb.
0·015 c.c. CO_2	1·209 c.c. CO_2
3·628 „ N	1·321 „ N
0·084 „ O	0·016 „ $(H_2 + O_2)$

There was a distinct evidence of the helium spectrum; the D_3 line was observed, but the tube "ran out" almost at once.

The next analysis was made on February 9, 1909. In this experiment it had been thought advisable to fill up the capillary tube with mercury, in order to avoid any possible contact between the thorium solution and the grease of a stop-cock. The presence of this mercury produced a very considerable change in the conditions of the experiment, for no less than 180 c.c. of gas were collected. This proved to be practically all pure nitrogen. A separation of the gas into its constituents was effected by cooling with liquid air under a pressure of two atmospheres, and then boiling off the nitrogen. In this way a residue was left behind which yielded on analysis 0·622 c.c. of carbon dioxide.

An examination of these figures makes it clear that carbon dioxide is present in the thorium bulbs in quantities which cannot be accounted for on any known basis. It is perhaps too soon to assume that carbon is a degradation product of thorium; but if we reject this solution, we have no other to put in its place.

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Experiments were now begun to test the action of radium emanation upon thorium nitrate solution. It was first shown that the emanation, when allowed to act upon tap-grease out of contact with oxygen, yielded only hydrogen, and not carbon dioxide. In addition to this, care was taken that the emanation never remained in contact with the grease of the tap in the apparatus for longer than a fraction of a second. It is thus possible to exclude the idea that carbon dioxide arises from the tap-grease. The first bulb was charged with thorium and emanation on June 3, 1908, and was opened on November 18 of the same year: 0·551 c.c. of carbon dioxide was found. The bulb was recharged with emanation and closed on November 20. When it was reopened on February 2, 1909, it was found that 0·124 c.c. of carbon dioxide was present. (A smaller quantity of emanation had been used in this experiment.)

Further experiments were now tried with zirconium nitrate, this metal being chosen on account of the fact that it belongs to the same family as thorium and carbon. Two bulbs were charged on August 19 and 26 respectively, and both were opened on November 20, 1908. In the one case it was found that 0·124 c.c. of carbon dioxide was present, while the second bulb yielded 0·116 c.c.

An experiment with hydrofluosilicic acid and radium emanation yielded 0·106 c.c. of carbon dioxide.

A crucial test was applied in the case of bismuth perchlorate. This substance was prepared by dissolving bismuth oxychloride in excess of perchloric acid, and evaporating the solution till it becomes syrupy and white fumes appear. The total amount of carbon dioxide present after the experiment had been carried out in the same way as the others was 0·150 c.c. Now, as the solution of bismuth perchlorate had been evaporated until perchloric acid fumes were evolved, it is clear that any organic matter whatever which was present in the bulb must have been oxidized, and therefore must have been removed with the chloric acid fumes. In this experiment no nitrogen was present, either as nitrite or nitrate in solution or in an elementary state in the gases evolved during the experiment. This proves that there was no trace of air leakage.

The following figures give the amounts of carbon in

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milligrammes produced by the action of one cubic millimetre of emanation in the case of each solution tested :—

Solution of	H_2SiF_6	$Tl(SO_4)_2$	$Zr(NO_3)_4$		$Th(NO_3)_4$		$Pb(ClO_3)_2$
			I.	II.	I.	II.	
Milligrammes of carbon	0·518	0·982	1·071	0·878	2·93	0·968	0·102

At the present time Ramsay considers that the matter is still *sub judice*, but there can be no doubt that even up to now the results are striking in the extreme. As he points out, we are quite in the dark as to the relative stabilities of the elements, and it may be that we have attacked the more stable ones up to the present time, instead of devoting our attention to ones which could be broken down by a smaller expenditure of energy. If, among the ordinary elements, we can hit upon some which border upon the radioactive condition without actually being active, it is quite possible that with the store of energy which the radium salts and emanation place at our disposal, we shall be able to overthrow the stability of their intra-atomic systems, and thus bring them in turn into the radioactive state. Much experimenting will be required before we can select the proper elements, if such exist.

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INDEX

NAMES

Abegg, 180
Alexandroff, 91
Ampère Electrochemical Company, 127
Angeli, 130, 131, 132, 136, 137
Arbuthnot, 60
Archibald, 18
Armstrong, 50
Arrhenius, 157, 175, 208

Baker, S. M., 157, 173
Baly, 46, 50, 51
Bamberger, 141
Bancroft, 208
Barker, 213
Barus, 94
Bary, 222
Baskerville, 213
Baur, 111
Becquerel, 204, 205, 209, 217, 222, 223, 224, 225
Berthelot, 116, 126, 178
Billitzer, 98, 103
Biltz, 185
Bingham, 111
Birkeland, 121
Blaise, 80
Blake, 98
Blomstrand, 145, 146, 149, 175
Bolley, 124
Boltwood, 215, 231, 232
Bragg, 220
Brauner, 185, 187, 188, 190
Bredig, 90, 97, 102
Bremer, 6
Briggs, 157
Brooks, 236
Brown, 95
Browning, 180
Brühl, 58
Büchner, 216
Bumstead, 236
Bunsen, 127

Cady, 110
Cameron, 240, 245, 246, 249
Campbell, 216
Carnelley, 61
Caro, 128, 141
Carrara, 110
Carrol, 110, 111
Caven, 162
Cavendish, 193, 194, 195
Centnerszwer, 110
Claus, 50
Collie, 50, 51, 52, 199, 200, 201, 238
Colson, 128
Cooke, 199, 202
Crommelin, 201
Crookes, 117, 185, 190, 191, 204, 220, 224
Crymble, 52, 53, 55, 58, 60, 61, 62, 63
Curie, P., 206, 223, 241, 244
Curie, Madame S., 206, 208, 209, 211, 218, 222, 223, 236, 239, 241, 249

Dammer, 180
Danne, 236
Davidson, 78
Debierne, 209, 211, 235, 239, 242, 244
Desch, 46
Desfosses, 127
Deville, 128
Dewar, 50, 197, 244
Divers, 107, 136
Dobbie, 51, 59, 63, 64
Donkin, 122
Donnan, 104
Dorn, 221, 235
Dowson, 128, 126
Duclaux, 94
Dunstan, A. E., 4, 8
Dunstan, W. R., 150
Dutoit, 110

Ebler, 216
Edminson, 58
Einstein, 97
Elster, 214, 215
Engelhardt, 55
Euler, 78, 80, 81, 83
Eyde, 121

Digitized by Google

Findlay, 9
Fleck, 124
Fownes, 127
Frank, 128
Franklin, 105, 106, 107, 108, 110
Friend, 156, 157, 173
Frowein, 6

Geitel, 214, 215
Giesel, 211, 215, 240, 244
Gimingham, 235
Glauber, 4
Gleditsch, 249
Glendinning, 58
Gonder, 215
Gore, 106
Gorke, 78
Goulding, 150
Graham, 86, 90, 91, 100
Gray, 235, 236, 237
Gruszkiewicz, 126
Guldberg, 118
Guye, 114

Haber, 122, 125, 137
Haga, 136
Hahn, 213, 214, 227, 232, 233
Halske, 117
Hampson, 198
Hantzsch, 71–88, 85
Hardy, 98, 102, 223, 224
Hartley, 46, 47, 48, 49, 50, 51, 55, 59, 65
Hemptinne, 122, 123
Henriot, 216
Herty, 164
Hertz, 200, 201
Hilditch, 58
Hillebrand, 195, 196
Himstedt, 244
Hinrichsen, 2, 6
Hofer, 116, 117
Hofmann, 212, 215
Hofmeister, 101
Holding, 198
Holleman, 71, 72
Howles, 117, 121
Hoyermann, 126
Huntington, 50, 51
Hutcheson, 125

James, 183
Jones, H. C., 13, 110, 111
Jones, H. O., 174
Jörgensen, 145, 147, 149, 150, 152, 154, 155, 156, 160, 165, 166, 167, 168, 169, 170, 171, 175

Kahlenberg, 110
Kaiser, 125
Kauffmann, 78, 79, 80
Kekulé, 50
Kennedy, 216
Konowalow, 71
Kraus, 105, 106, 108

Laborde, 208
Lachman, 71
Ladenburg, 50
Lambilly, 123, 124
Lauder, 63, 64
Lefebre, 116
Lepel, 116
Le Rossignol, 235
Levin, 216
Levier, 110
Ley, 55, 61
Linder, 95, 103
Lindsay, 13, 110, 111
Lockyer, 199
Lossen, 150

Mackenzie, 231, 248
Mackey, 125
Magini, 59
Mahler, 178
Makower, 236
Malfitano, 94
Marckwald, 210
Mathews, 110
McCoy, 231
McDougall, 117, 121
McLennan, 216
McMaster, 111
Mehner, 129
Meissner, 116
Mendeléeff, 193
Meyer, 244
Meyer, V., 70
Michael, 71
Miolati, 161
Mohr, 2
Moissan, 180, 202
Moore, 202
Müller, 9
Muller, 84
Muthmann, 116, 117, 177, 178

Nernst, 117, 118, 120
Nithack, 128

Ober, 103
Odling, 146
Olszewski, 197, 201
O'Neill, 126
Onnes, 199
Ostwald, W., 208
Ostwald, Wo., 86, 87, 100
Ouvrard, 201
Owens, 234

Digitized by Google

Palmieri, 199
Pascal, 58
Paschen, 220
Pasteur, 8
Pauli, 94
Perkin, Sir W. H., 58
Petersen, 163, 164, 165
Pickering, 238
Picton, 95, 108
Piloty, 137, 150
Playfair, 127
Precht, 208, 209
Prim, 116

Ramsay, 96, 122, 157, 158, 159, 193, 194, 195, 196, 197, 199, 201, 202, 208, 213, 235, 236, 237, 238, 239, 240, 241, 243, 244, 245, 246, 249, 252
Rayleigh, 116, 117, 194
Rea, 58
Regnault, 122
Reitzenstein, 146
Retgers, 2, 185
Reychler, 185
Rillet, 55
Röntgen, 204, 205
Roozeboom, 9
Roscoe, 105
Royds, 249
Rudorf, 185
Ruer, 216
Ruff, 150
Ruhoff, 110
Runge, 208, 209
Rutherford, 210, 215, 218, 219, 220, 224, 225, 226, 227, 230, 231, 232, 234, 236, 238, 239, 242, 243, 244, 249

Sabanejeff, 91
Sachse, 50
Sachsel, 2, 6
Sackur, 214
Scacchi, 8
Schlundt, 110
Schlutius, 123
Schmidt, 205
Schmoluchowsky, 97
Schneider, 94
Schönbein, 187
Schönrock, 14
Schorlemmer, 105
Schultze, 71, 72
Schutzenberger, 128
Siemens, 117
Smiles, 58
Smoluchowsky, 95
Soddy, 224, 225, 231, 239, 240, 241, 243, 244, 245, 248
Soret, 55
Spiegel, 157
Spiro, 101
Spring, 108
Staedel, 8
Stafford, 108
Steele, 185
Stewart, 52, 53, 55, 58, 59, 60
Strauss, 212, 215
Strong, 216
Strutt, 217, 219, 231
Sudborough, 223
Svedberg, 96

Thiele, 56, 57
Thole, 4, 8
Thomsen, 50
Thorpe, 209
Tinkler, 63, 64
Travers, 193, 197, 198, 199, 201, 202
Troost, 201
Tschirner, 141

Usher, 249
Usiglio, 19, 20

Van Bemmelen, 100
Van't Hoff, 8, 9, 19, 20, 23, 26, 27, 29, 33, 34, 36, 37, 39, 163, 203
Vavon, 216
Vergara, 115
Voegelen, 82

Waage, 118
Walden, 110, 163
Watson, 199, 200, 201, 202
Watts, 209
Weiss, 177, 178
Welsbach, 177, 211, 212, 215
Werner, 151, 152, 153, 154, 155, 156, 157, 161, 164, 165, 166, 167, 168, 169, 170, 171, 173, 174, 175
Wheeler, 236
Whetham, 231
Whitney, 93, 103
Willcock, 223
Williams, 195
Wöhler, 123
Wölfl, 215
Woltereck, 124
Wright, 53, 55, 58, 60
Wurtz, 146
Wyrouboff, 3

Young, 122

Zerban, 212, 213

Digitized by Google

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INDEX

SUBJECTS

Abnormal hydrates, 75, 82
" hydrolysis, 77
" temperature coefficients, 80
Absorption band, 46
" " head of, 46
" " persistence of, 47
" general, 46, 53 ff.
" selective, 46
" spectra, 41 ff.
" " and chemical reactions, 65
" " " isomeric change, 55
" " " linkage-change, 55, 58
" spectrum, definition of, 42
" " factors influencing, 44
" " method of plotting, 46
" " of benzene, 50 ff.
" " of benzoquinone, 44, 47 ff.
" " of cotarnine, 63
" " of ferric chloride, 42, 46
" " of hydroxycarbanil and of its derivatives, 48
" " of quinone 44, 47
Acetamide, 106, 108
Acetic acid, conductively of, 83
Acetoacetic ester, 47 ff.
Acetohydroximic acid, 138
Acetylacetone, derivatives used in rare earth separations, 183
Acetylenic linkage and general absorption, 55
Aci-forms, 71 ff.
Actinium, 207, 211, 228, 232, 249
" A, 228
" B, 228
" emanation, 228, 232, 235
" identical with emanium, 211
" isolation of, 211
" X, 228
Active deposit of radium emanation, 229, 243
Activity, equations for decay and recovery of, 225
" excited, 241
" induced, 212
Additive properties, 41
Affinity, residual, and general absorption, 58, 60
" " " 58, 60, 67
Alcogel, 86
Alcosol, 86
Aldehyde reaction of Angeli, 133, 136, 137, 141
Alkalis, strength of, estimated by spectroscope, 63

Digitized by Google

Alkyl bromides, absorption spectra of, 54
Alkyl iodides, their action on nitroxyl, 138
Alpha-particles, 221, 226, 227
Alpha-rays, 218, 219, 225
,, influence of magnetic field on, 219
,, nature of, 219, 221
Amines, action of nitroxyl on secondary, 139
,, oxidation of, 141
Ammonia and its hydroxyl derivatives, 141 ff.
,, decomposition of, 143
,, liquid, properties of, 105
,, ,, reactions in, 105 ff.
,, manufacture of, 122 ff.
,, production of, from nitroxyl, 138
,, reaction for pseudo-acids, 75, 81
Ammonium salts, co-ordination ideas applied to, 173
,, ,, disproof of Werner's ideas on, 174
,, sulphate, 2
Ammonio-acids, 106, 108
Ammonobasic salts, 110
Ammono-bases, 106, 108
Ammonolysis, 109
Ammonolytic reactions, 110
Ammono-salts, 106, 108
Amphoteric electrolytes, 69
Angeli's aldehyde reaction, 133, 136, 137, 141
Anhydrite, 18
Antimony chlorides, 68
Antozonides, 187
Aqueous-alcohol solutions, conductivity of pseudo-acids in, 82
Aquopentammine salts, 166
Arc spectra, 185
Argon, 193, 195, 201,
,, attempts to prepare compounds of, 202
,, isolation of, 195
,, produced from radium emanation, 246
,, properties of, 202
,, specific heats of, 195
Armstrong's quinonoid hypothesis, 42
Arsenic sulphide sol, 95
Ascherite, 35
Astrakanite, 9, 10, 11, 12, 35, 36, 37, 38
,, solution of, in water, 9 ff.
"Atomare" union, 151
Atomic weight, influence of, on double salt formation, 2
,, ,, of radium, 208
Auxiliary valencies, 151
,, ,, confusions arising from conception of, 154
,, ,, definition of, 151
Auxochroma hypothesis, 79

Bacteria, action on nitrogen in nature, 114
Baker's views of cobaltammines, 157, 173
Band, absorption, 46
,, head of absorption, 46
,, persistence of absorption, 47
Barium cyanamide, 128
,, platinocyanide, 222
Bases, strength of, estimated spectroscopically, 63
Basicity method of isolating rare earths, 182

Digitized by Google

Becquerel rays, 204, 209, 217 ff., 224
,, ,, chemical effects of, 223
,, ,, influence of electro-magnet on, 217 ff.
,, ,, nature of, 217 ff.
,, ,, physical effects of, 222
,, ,, physiological effects of, 223 ff.
,, ,, properties of, 204, 217 ff.
Benzaldoximes, spectra of, 59
Benzene, Collie's space formula for, 50
,, formulæ proposed for, 50, 57
,, spectrum of, 50 ff.
,, ,, ,, hexasubstituted derivatives, 52
,, sulphohydroximic acid, hydrolysis of, 137
Berzelius', views of cobaltammines, 146
Beta-rays, 218, 225
,, influence of magnetic field on, 218
,, nature of, 219, 220
,, photographic effect of, 219
,, velocity of particles in, 221
Bischofite, 36. *See also* MAGNESIUM CHLORIDE.
Bismuth perchlorate, 251
Blomstrand's views of cobaltammines, 145 ff.
Borates, 37
Brassidic acid, 60
Brauner's views on rare earths, 188 ff.
Bredig's inorganic ferments, 97
,, method of colloid preparation, 90
Bremer-Frowein tensimeter, 6, 34
Bröggerite, 199, 212
Bromate method of rare earth separation, 184
Bromine addition to double bonds, 56 ff.
Bromopentammine salts, 147
Brownian movement, 95

CÆSIUM, 185
,, chloride, 2
Calcium cyanamide, 128
,, salts, van't Hoff's work on, 37
,, sulphide, 222
Canal-rays, 221
Carbamide, 106
Carbides used in fixation of nitrogen, 127
Carbonatotetrammino cobalt bromide, 165
,, ,, ,, chloride, 167
Carnallite, 18, 23 ff., 26, 27, 34, 36
Carnotite, 215, 232
Caro's reagent, 141
Catalysis in fixation of nitrogen, 123
Cataphoresis, 94, 102
Cathode rays, velocity of, 221
Cavendish's researches, 193
Cell of spectroscope, 43
Cerium, 176, 178, 179, 181, 184
,, group, 176, 180
Chalcolite, radioactivity of, 206
Chemical change, spectroscopic determination of, 63
,, reactions and absorption spectra, 65
Chili, nitre beds of, 114
Chloronitrito-diethylenediammino derivatives, 170 ff.
Chloronitrotetrammino cobalt chloride, 165

Digitized by Google

Chloropentammine salts, 147
Chromium chlorides, 62
Citraconic acid, 58, 59, 60
Cleveite, 196, 199, 212
Coagulation, 88, 97 ff.
,, of globulin by Becquerel rays, 224
,, reversible and irreversible, 98
,, -temperature, 99
Cobaltammines, 144 ff.
,, chemical behaviour of, 160 ff.
,, conductivities of their solutions, 161 ff.
,, molecular volumes of, 148
,, ,, weights of, 147
,, number of ions in their solutions, 160 ff.
,, theories of, 145 ff.
Cobalt chloride, 61, 144
,, salts, colours of, 61
Cobaltion, 160
Colemanite, 35
Collie and Baly's researches, 50 ff.
Collie's benzene formula, 50
Colligative properties, 41
Colloids, 86 ff.
,, classification of, 87
,, coagulation of, 88
,, conductivities of their solutions, 93
,, diffusion of, 91
,, ferment-like action of, 97
,, molecular weights of, 91
,, nomenclature of, 87
,, poisoning of, 97
,, preparation of, 89 ff.
,, properties of, 91 ff.
,, size of particles in, 87, 93
,, theories of their nature, 99 ff.
Colour, origin of, 66
,, physiological, 42
Coloured salts of colourless acids, 78 ff.
Complex salt, 1
Compressibilities of gases,
Conductivity measurements in cobaltammine series, 161 ff.
,, ,, colloid solution, 93
,, ,, pseudo-acid problem, 73, 75
,, ,, proving presence of double salts, 13
,, method of determining i, 163 ff.
Conglomerates, 1, 14, 15
Conjugated double bonds, 57 ff.
Constant, solution, 21
Constitution and conductivity, 73, 76, 161
Constitutive properties, 41
Cooke's researches on rare gases, 199
Co-ordination, 153
,, confusions involved in conception of, 154, 174
,, example of assumptions required for, 154
,, its application to ammonium salts, 154
,, ,, ,, oxonium salts, 154
,, Jörgensen's criticism of, 154
,, numbers of oxalyl radicle, 155
Copper iodide, 61
,, sulphate, 62
,, ,, action of radium emanation on, 246 ff.

Digitized by Google

Cotarnine, 68
Croceo cobalt nitrate, 165
Croceo-salts, 167
Crooke's conception of non-homogeneous elements, 191
,, meta-elements, 190
,, tube, 204
,, views on rare earths, 190 ff.
Crymble's views, 61 ff.
Cryoscopic determination of *i*, 163
,, measurements applied to double salt problem, 14
Crystallization, end-point of, 28
,, fractional, 182
Crystalloids, 86
,, diffusion of, 91
Cupric chloride, 13, 62
,, lithium chloride, 13
Curie (Mme.), researches of, 206
Curves of molecular vibration, 46
,, plotting of, 46
Cyanamide, 128
Cyanides, production of, 125 ff.
Cyclic bodies, general absorption of, 55

Decay of thorium X, 225
Dialysis, 90
Diamagnetism, 58
Diammine series, 145
Diamond, action of Becquerel rays on, 222
Diazo-hydroxides, formation of, 139
Diazomethane, 48
Dichloro-diethylenediammino salts, 172
Dichloro-tetrammino salts, 172
Didymium, 181
Dielectric constant, 41
Diethylenediammine salts, 166 ff.
Differential tensimeter, 6, 34
Diffusion velocities of colloids and crystalloids, 91
Dihydroxy-ammonia. *See* Nitroxyl.
Dihydroxylamine hydrochloride, 150
Dilatometric determination of transition point, 4
Dinitro-diammin-dinitro-diammin-oxalate, 154
Dinitro-diammin-oxalate, 155
Dinitro-ethane, 77
Dinitro-methane, 81
Dinitro-tetrammino salts, 170, 172
Dinitro-triammino cobalt chloride, 165
Disintegration hypothesis, 224 ff.
Disperse phase, 87
Dispersion medium, 87
Dispersoid, 87
Dobbie, Lauder, and Tinkler's researches, 63 ff.
Double bonds, conjugated, 57 ff.
Double salt formation used in rare earth purification, 180–181
,, ,, influence of atomic weight on, 2
,, ,, ,, of pressure on, 2
,, ,, ,, of temperature on, 3, 35 ff.
,, salts, 1 ff.
,, ,, conditions of their formation, 2
,, ,, existence limits of various, 36
,, ,, in solution, 18

Digitized by Google

Dowson gas, 123,
Dysprosium, 176, 181, 184

Eka-aluminium (gallium), 193
Eka-boron (scandium), 193
Eka-silicon (germanium), 193
Electrical osmosis, 94
Electric arc, 116
Electrolytes, amphoteric, 69
Electrolytes, classification of, 69
Electrolytic action in fixation of nitrogen, 123
Electro-magnet applied to arc, 121
Electromotive force, method of transition point determination, 4, 8
Electronic view of cobaltammines, 158 ff.
Electrons, 158 ff., 220
,, as atoms of electricity, 158
Electroscope, 206, 217
Elements, Crookes' view of, 190 ff.
Emanation of thorium, 234
Emanations, radioactive, 234. *See also under respective elements.*
Emanium. *See* Actinium
Empirical rule of Werner and Miolati, 161
Emulsin, 97
Emulsoids, 88
End-point of crystallization, 23
en-form, 158
Erbium, 176, 179, 181, 184
Erucic acid, 60
Ethyl nitrite, 70
Ethylene diamine cobalt derivatives, 166
,, ,, derivatives, Jörgensen's explanation of their isomerism, 169
Ethylenic linkage and general absorption, 55, 59
Euler's views on pseudo-acids, 81, 83
Europium, 176, 181
Excited activity, 241
ex-form, 158

Fergusonite, 199
Ferric chloride, 2, 6, 13, 42, 62, 144
Ferric hydrosol, 98
Ferrous chloride, 62
,, sulphate, 2
Five salts in solution, case of, 31 ff.
Fixation of nitrogen, 113 ff.
Flavo cobalt nitrate, 165
Flavo-salts, 167
Fluorescence produced by radio active bodies, 222
Fluorspar, 223
Fractional crystallization, 182
,, precipitation, 182
Freezing-point depression with double salts, 14
Frequencies, 44
Friend's explanation of cobaltammines, 156, 173
,, views on valency, 156
Fumaric acid, 59, 60

Gadolinium, 176, 179, 181
Gallium, 193

Digitized by Google

Gamma-rays, 218, 219
,, influence of magnetic field on, 219
,, nature of, 220
,, penetrative power of, 219
Gel, definition of, 86
Gelatine, 99
General absorption, 46, 53 ff.
,, ,, factors affecting, 54 ff.
Geological thermometer, 39
Geometrical isomers, general absorption of, 59
,, ,, unaffected by radium, 223
Germanium, 193
Glaserite ($2K_2SO_4$, Na_2So_4), 35, 38
Glass, action of Becquerel rays on, 222
Glauberite, 35
Glauber's salt, 4, 36, 37
Globulin, coagulation of, 223
Glutaconic ester, 80
Gold hydrosol, size of particles in, 93
Gold iodide, 61
Gypsum, 35

Halogen atoms, properties of, in pentammine salts, 147
Hantzsch's pseudo-acid criteria, 74
Hartley's method, 47 ff., 65
,, vibration curves, 46
Head of absorption band, 46
Heat, evolved by radium, 208
,, its lack of influence on radioactive changes, 226
Helium, 196
,, isolation of, 196
,, liquefaction of, 199
,, occurrence of, 199
,, origin of, in mineral springs, 199, 245
,, possible compounds of, 199–200
,, production of, from radium emanation, 243 ff.
,, properties of, 199
,, spectrum, 196, 199, 200
Hertz waves, 200, 201
Hexammine series, 145
Holmium, 176, 179, 181, 184
Homologous series, absorption spectra of, 54
Hydrates, abnormal, 75
Hydrazine, its action with nitroxyl, 140
Hydro-acids, 106
Hydro-bases, 106
Hydrocyanic acid, 97
Hydrofluosilicic acid, action of radium emanation on, 251
Hydrogel, 86
Hydrolysis, abnormal, 77 ff.
Hydro-salts, 106
Hydrosol, 86
Hydroximic acids, formation of, 133, 136
,, ,, hydrolysis of, 134
Hydroxycarbanil, 48, 49, 50
Hydroxylamine, its action with nitroxyl, 140, 143
,, oxidation of, 138
,, preparation of, from nitroxyl, 138
,, reducing and oxidizing action of, 137
,, salts, 150

Digitized by Google

Hydroxylamine, substitution products, 139
,, sulphonic acid, hydrolysis of, 186
Hydroxyl derivatives of ammonia compared, 141
Hyponitrite formation, mechanism of, 133
Hyponitrites from nitrohydroxylaminic acid, 133

i, 163 ff.
Inactive gases, 193 ff.
Incandescent mantle industry, 177
Indicators, action of phosphoric acid with, 162
Indium, 185
Induced activity, 212
Inert gases. *See* INACTIVE GASES
Iodoform broken down by radium, 223
Ionium, 215, 232, 233
Ionization and chemical constitution, 161
,, in pentammine series, 148
,, media, non-aqueous, 110 ff.
,, of gases by Becquerel rays, 228
Ions, coagulating action of, 98
,, Crymble's views on absorptive power of, 61 ff.
,, in cobaltammine solutions, 160 ff.
Iron group, anomaly in, 144
Isoelectric state, 102
Isolation of radium, scheme of, 207
,, rare earth elements, 180 ff.
Isomeric change, and absorption spectra, 55, 58, 59, 66
Isomers, geometrical, not affected by radium, 223
Isosafrol nitrosite, 186
Itaconic acid, 58

JAMES' methods of rare earth separation, 183
Jörgensen's criticisms of Werner's ideas, 154, 165 ff.
,, explanation of ethylene diamine derivatives' isomerism, 169
,, oxonium salts, 150
,, researches on cobaltammine structures, 147 ff.
,, views of cobaltammines, 145 ff.
Jörgensen-Werner controversy, 165 ff.

KAINITE, 34, 35, 36, 38
Kieserite, 18, 34, 36, 37, 38
Krypton, 197, 202
,, isolation of, 197
,, properties of, 202

LACTAM and lactim forms, 48, 49
Laevulinic acid, 88
Langbeinite, 36, 37
Lanthanum, 176, 177, 178, 179, 181, 184, 185, 211
Latent valency, 156
Lead imide, 106
Lead, radio-activity of, 215
Lecithine, breakdown of, 223
Leonite, 34, 35, 36, 37, 38
Linkage change and absorption spectra, 49
Lithium, chloride, 13, 43
,, produced from copper sulphate, 246 ff.

Digitized by Google

Loewite, 36, 38
Lutecium, 176
Luteo-cobalt chloride, 144

Magnesium chloride, 21, 23, 24, 25, 26 ff., 34
,, sulphate, 2, 9, 10, 11, 12, 21, 26 ff., 34
,, ,, heptahydrate, 26, 34, 37, 38. *See also* Reichardtite
,, ,, hexahydrate, 26, 27, 37
Magnetic rotation, 58
,, ,, application to double salt problem, 14
Main valencies, 151
,, ,, confusions arising from conception of, 154
,, ,, definition of, 151
Maleic acid, 59, 60
Manganese sulphates, 62
Mean valency, 35
Melting-points as criteria of nature of equimolecular mixtures of optical antipodes, 15 ff.
Mercuric chloride, 151
,, cyanide, 151
,, nitride, 106
Mercury nitrate, 250
Mercury succinimide, 108
Mesaconic acid, 58, 59, 60
Mesotartaric acid, 59
Mesothorium, 214
Michael's views, 71
Meta-elements of Crookes, 190
Microbalance, 237–8
Mixed crystal and double salt, relations between, 2
,, crystals, 1, 14, 15
Model, three dimensional, 29 ff.
,, ,, ,, simplification of, 31, 33
Mohr's salt, 2
Molecular vibration curves, 46
,, weight of colloids, 91
Molybdenum, 188
Monazite sand, 177, 213, 232
Moore's examination of liquid air residues, 202

Negative valency, 156
Neodymium, 176, 178, 179, 181, 188
Neon, 197, 200
,, isolation of, 197
,, luminescence phenomena of, 201
,, produced from radium emanation, 246
,, properties of, 200
,, spectrum of, 200
Neo-ytterbium, 176
Nernst's researches, 117 ff.
Neutralization, slow, 74, 76
Nickel chloride, 144
,, salts, colours of, 61
Niton. *See* Radium emanation
Nitre-beds of Chili, 114
Nitric acid, production of, 115 ff.
,, oxide, 117 ff.
,, ,, Nernst's researches on, 117 ff.
Nitrides, production of, 128

Digitized by Google

Nitrito-nitrato-diethylenediammino derivatives, 170
Nitro-ethane, 70, 76
Nitrogen, Rayleigh's researches on, 194
,, fixation of, 112 ff.
,, its circulation in nature, 112
,, oxides, production of, 115 ff.
Nitro-groups, isomerism in, 166, 170
,, negative character of, 70
Nitrohydroquinone ether, 79, 80
Nitrohydroxylaminic acid, 130 ff., 138
,, ,, ,, decompositions of, 132 ff.
,, ,, ,, hyponitrites from, 133
,, ,, ,, salts of, 131
Nitromethane, 71
Nitroparaffins, 70 ff.
Nitrophenol ethers, 78
Nitrosites, formation of, 136
Nitrosoderivatives, action of nitroxyl on, 139
Nitrous acid, production of, 115 ff.
Nitroxyl or dihydroxy-ammonia, 135
,, its action on amines, 139
,, ,, on hydroxylamine and hydrazine, 140
,, ,, on nitroso-bodies, 139
,, oxime formation with, 138
,, preparation of, 135
,, reactions of, 138 ff.
,, reduction of, 138
,, structure of, 141
Non-colligative properties, 41
Non-separable activity, 227

Octahedral arrangement, Werner's, 153
"Onium" salts, 66
Optical antipodes, criteria of nature of mixtures, 14 ff.
,, ,, general absorption of, 59
,, properties of colloids, 90
,, rotary power, 58
Osmosis, electrical, 94
Osmotic pressure, 91
Oxalyl radicle, quadrivalent on Werner's hypothesis, 155
Oxime formation with nitroxyl, 138
Oxonium salts in cobaltammine series, 150
,, ,, Werner's ideas on, 154
Ozone formed by action of radium, 223
Ozonides, 187

Parageneses, diagrams of, 39, 40
,, table of, 38
Paragenesis, 35 ff.
Partial valencies, 56
Particles, size of, in colloids, 93
Pasteur's researches on racemates, 3
Pentammine salts, two sets of halogen atoms in, 147-8
,, series, 145, 147, 165
Periodic System or Table, 185, 193, 196, 198, 209 ff.
,, ,, anomalies in, 185
Peroxides, types of, 187
Persistence of band, 47
Petersen's criticism of Werner, 163
,, researches, 163 ff.
Phenol and water, solutions of, 100

Digitized by Google

Phenolphthalein, behaviour of liquid ammonia, 107, 108
Phenylnitramine, 81, 83
Phenyl-nitromethane, 72
,, ,, ethers, 78
Phosphorescence spectra, 185
Phosphoric acid, 162
Phosphorus trichloride, 162
Physical properties, classification of, 41
Physiological colour, 42
Picramide, 109
Pitchblende, 205, 230, 231
Plate, standard, 43
Platin ammonia salts, 146
,, ,, ,, ferment-like action of, 97
Platinum hydrosol, coagulation of, 103
,, ,, conductivity of, 94
,, ,, size of particles in, 93
Poisoning of colloids, 97
Polarisation of light in colloid solutions, 92
Polonium, 207, 210. *See also* RADIUM F
,, atomic weight of, 210
,, isolation of, 207
Polyhalite, 18, 19,
Polyoxides, 187
Positive valency, 156
Potassamide, 108, 109
Potassium, radioactivity of, 216
,, acetamide, 106
,, chloride, 6, 13, 21, 22, 23, 24, 25, 26 ff., 34, 38
,, nitrate, 106
,, sulphate, 2, 26 ff., 34
,, uranium sulphate, 204
Praseodymium, 176, 178, 179, 181, 188
Praseopurpureo salts, 167, 168
Praseoroseo salts, 168
Praseo-salts, 167
Precipitation, fractional, 182
Pressure, its influence on double salt formation, 3
Pseudo-acids, 69 ff.
,, ,, criteria of, 74 ff.
,, ,, definition of, 74
,, ,, properties of, 78
Purpureo salts, 167
Pipyridine, two molecules monomolecular on Werner's hypothesis, 155

QUINONE, spectrum of, 44
Quinonoid hypothesis, 42

RACEMIC compounds, melting-point phenomena of, 14
,, ,, general absorption of, 59
Radiation of thorium X, 227
Radioactive change, 217 ff.
,, ,, different from chemical reaction, 226
,, ,, equations for its velocity, 225
,, ,, uninfluenced by heat, 226
,, elements, 208 ff.
,, emanations, 234 ff. *See also under respective elements*
Radioactivity an atomic property, 226
Radio-lead or Radium D, 215, 229

Digitized by Google

Radio-thorium, 214
Radium, 205 ff., 230–233, 249
,, and uranium, co-occurrence in ores, 231
,, atomic weight of, 208, 209
,, bromide, 207, 226
,, carbonate, 226
,, chloride, 206, 209
,, half-life period of, 230, 233
,, metallic, 209
,, origin of, 230 ff.
,, parent substance of, 216, 230 ff.
,, scheme of isolation process, 207
,, source of its energy, 224
,, A, 229
,, B, 229
,, C, 229
,, D or radio-lead, 215, 229
,, E_1, 229
,, E_2, 229
,, emanation, 229, 234 ff.
,, ,, active deposit of, 229
,, ,, chemical inertness of, 239
,, ,, decomposition of, 241 ff.
,, ,, its action on hydrofluosilicic acid, 251
,, ,, on hydrochloric acid, 245
,, ,, ,, on water, 240, 245
,, ,, method of manipulating, 236
,, ,, one of the inactive gas series, 237
,, ,, physical properties of, 236
,, ,, production of helium from, 243 ff.
,, ,, quantity of, evolved, 236, 239
,, ,, radioactive properties of, 240
,, ,, Ramsay and Soddy's researches on, 243 ff.
,, F, 210, 229. *See also* POLONIUM
,, salts, heat evolved by, 208
,, ,, properties of, 207 ff.
,, ,, properties of their solutions, 208
,, ,, spectra of, 208
Ramsay and Rayleigh, isolation of argon, 195
,, ,, Cameron's researches on transmutation, 245 ff.
,, ,, Soddy's production of helium from radium emanation, 243 ff.
,, ,, Young on decomposition of ammonia, 122
Ramsay's view of Brownian movement, 96
,, views of cobaltammines, 158
Rare earth elements, carbides of, 179
,, ,, ,, chemical character of, 178 ff.
,, ,, ,, heats of combustion of, 178
,, ,, ,, hydrides of, 179
,, ,, ,, nitrides of, 179
,, ,, ,, oxides of, 179
,, ,, ,, physical properties of, 177 ff.
,, ,, ,, their place in the Periodic Table, 185 ff.
,, earths, 176 ff.
,, ,, importance of, 177
,, ,, occurrence of, 176, 177
,, ,, purification of, 180 ff.
Rayleigh and Ramsay, isolation of argon, 194, 195
Rayleigh's work on nitrogen density, 194
Rays. *See* ALPHA-, BETA-, GAMMA-, X-, and BECQUEREL.
Reactions and absorption spectra, 65
,, spectroscopic study of, 66

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Reaction-velocities, action of solvent on, 66
Recovery of thorium X activity, 225
Refractive index, 41, 58, 88
Refractivity criterion for pseudo-acids, 88
Reichardtite, 36, 37. *See also* MAGNESIUM SULPHATE HEPTAHYDRATE
Researches, suggested, 65 ff.
Residual affinity, 58, 60, 67
,, ,, and general absorption, 58, 60
,, ,, in chemistry, 67
,, valency, 156
Röntgen rays, 204. *See* X-RAYS
Roseo-cobalt chloride, 144
Roseo-salts, Werner's explanation of supposed isomerism, 166
Rubidium racemate, 9
Rubidium, radioactivity of, 216
,, tartrates, solubility relations of, 9
Rule, van't Hoff's, 23
Rutherford's views of radioactive change, 226

SALT deposits, problem of, 18 ff.
Samarium, 176, 178, 179, 181
Samarskite, 212
Santonine, 42
Scandium, 176, 179, 181, 185, 198
Schönbein's ozonides and antozonides, 187
Schönite, 27, 35, 36, 37, 38
Sea-water, evaporation of, 20
Selective absorption, 46
Silent discharge, 116, 117, 122
Silicic acid, 86, 99, 100, 101
Silicon nitride, 128
,, nitride-carbide, 128
Silver hydrosol, size of particles in, 93
,, iodide, 61
Silver nitrohydroxylaminate, 133
Size of colloid particles, 98
Slow neutralization, 74
Sodamide, reaction with acetamide, 108
Sodium acetamide, formation of, 108
,, ammonium racemate, 3
,, chloride, 2, 18, 21, 22
,, iodide, 61
,, nitrohydroxlyaminate, 131, 132, 133, 134, 135
,, ,, ,, constitution of, 132
,, succinimide, 106
,, sulphate, 9, 10, 11, 12, 21
Sol, definition of, 86
Solubility method of determining transition points, 4, 6
,, ,, of separating rare earth elements, 181, 182
,, relations of rubidium tartrates, 9
Solution, constant, 21
Solvent action and absorption spectra, 65
Space formula of benzene, 50
,, models of solutions, 29, 32
Spark discharge, 116, 117
,, spectra, 185
Spectra, absorption, 41 ff. *See also* ABSORPTION SPECTRA
,, arc, 185
,, phosphorescence, 185
,, spark, 185
Spectrometric method of determining transition points, 4, 6

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Spectroscope applied to rare earth isolations, 184
,, arrangement of, 42 ff.
Spectroscopic determination of chemical change, 63
Spectroscopy, its relation to chemistry, 67
Spectrum of helium and mercury, 200
Spinthariscope, 221
Standard plate, 43
Stassfurt salts, 18 ff.
Stimulation of one atom by another, 66
Substituents, influence of, on benzene vibrations, 52–3
Substitution, effects of, on spectra, 43, 52–55
Succinimide, 106
Sulphamide, 106
Sulphonyl derivatives of hydroxylamine, 136, 137
Superoxides, 187
Supersaturation of solutions, 34
Suspensoids, 88
Suspensions, 87
Sylvine (potassium chloride), 35, 36
Symmetry of benzene destroyed by substitution, 52
,, ,, molecule and general absorption, 55

Table of basicities found by Dobbie, Lauder and Tinkler, 64
,, of double salt existence-limits, 38
,, of parageneses, 39–40
,, of radium degradation products, 229
,, of supposed numbers of ions in cobaltammine solutions, 165
,, of uranium, thorium, actinium, and degradation products, 228-9
,, rearrangement of, Brauner's Periodic, 189
,, showing radium extraction process, 207
Tantalum, 185
Tartaric acids, general absorption of, 59
Tellurium and polonium allied, 210
Temperature coefficients, abnormal, 80
Temperature, influence of, on double salt crystallization, 35 ff.
,, influence on double salt formation, 3, 35 ff.
Tensimeter, 6, 34
Tensimetric determination of transition point, 4, 5 ff.
Terbium, 176, 179, 180, 181
,, group, 176
Tetrammine series, 145
Tetramminopurpureo salts, 167
Tetramminoroseo salts, 167
Tetrazones, formation from nitroxyl, 139
Thallium salts, 68
Thenardite, 36, 37, 38
Thermometer, geological, 39
Thermometric determination of transition point, 4, 6
Thiele's theory of partial valencies, 57
Thorianite, 213
Thorium, 180, 205, 212 ff., 216, 225, 226, 227, 228, 242
,, atom, disintegration of, 226
,, non-separable activity of, 227
,, A, 228
,, B, 228
,, emanation, 227, 228, 234, 242
,, ,, conversion into solid substance, 228
,, ,, half life period of, 227–30
,, nitrate, 249, 251
,, separation from actinium, 211

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Thorium, X, 225, 227, 228
,, X, radiation of, 227
Thorium-1 ek., 214, 227–8
Thulium, 176, 179, 181
Time, influence of, in salt deposition, 34 ff.
Tin chlorides, 68
Transition interval, definition of, 13
,, intervals, 8 ff.
,, definition of, 13
,, point, determination of, 4 ff.
,, temperature, 3 ff., 35 ff.
,, ,, of astrakanite, 10
,, ,, of ferric potassium chloride, 6
,, ,, of rubidium racemate, 9
,, of sodium ammonium racemate, 3
Transmutation, 245 ff.
Triammine series, 145
Triammino cobalt nitrite, 159
Triboluminescence, 221
Trielectride of cobalt, 160
Trihydroxylamine hydriodide, 150
Tungsten, 188

Ultramicroscope, 92
Unsaturation, its influence on general absorption, 55 ff.
Uranium, 196, 204, 205, 206, 207, 212, 213, 216, 224, 225, 229, 231, 232, 233
,, and radium, co-occurrence of, 231
,, X, 224, 225, 229
Usiglio's researches, 19 ff.

Valency, auxiliary, 151
,, free negative, 156
,, ,, positive, 156
,, latent, 156
,, main, 151
,, mean, 35
,, partial, 56
,, residual, 156
,, and light absorption, 61 ff.
Vanthoffite, 36
Van't Hoff's equation, 163
,, ,, factor *i*, 163 ff.
,, ,, researches on oceanic deposits, 19 ff.
,, ,, Rule, 23
,, ,, space model, 29 ff.
Vibration curves, Hartley's, 46
Violeo- and praseo-salts, confusion between the series, 168–9
Violeo-purpureo salts, 167
Violeo-roseo salts, 168
Violeo-salt, Werner's typical, a praseo-compound, 169
Violeo-salts, 169
Violuric acid, 83
Viscosity method of determining transition points, 4
,, of colloid solutions, 88
Visible spectrum, 42

Walden's researches, 111
Water of crystallization, 4
Werner and Miolati's empirical rule, 161
Werner's conductivity measurements, 161

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Warner's explanation of cobaltammines, examples of exceptions to, 154, 155, 165, 166, 167, 168
,, hypothesis, 151 ff.
,, ,, bases of, 151
,, ,, Jörgensen's criticism of, 154, 165 ff.
,, ,, of ammonium and oxonium salts, 154, 173
,, typical violeo-salt a praseo-compound, 169

Xantho-salts not explicable on Werner's hypothesis, 165
Xenon, 185, 198
,, isolation of, 198
,, properties of, 202
X-rays, 204, 205, 217, 220, 224

Ytterbium, 176, 179, 181
,, group, 176, 180
Yttrium, 176, 181, 183, 184, 185
,, group separation, 183–4

Zinc sulphate, hydrates of, 2, 8
,, sulphide, 221
Zirconium nitrate, 252

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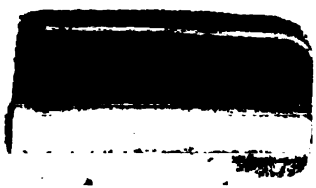

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